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POLAROGRAPHIC BEHAVIOUR OF METAL CHELATES OF *o,o'*-DIHYDROXYAZO DYES

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Summary—The nature of complexes between various *o,o'*-dihydroxyazo dyes and metal ions, and their applications in polarographic chemical analysis, are described and discussed.

IN 1950, Willard and Dean[1] discovered that the single polarographic wave of Mordant Violet 5 was split into two reduction waves in the presence of aluminium ions. The height of the second wave, which was about 0·2 V more negative than the first, was found to be proportional to the aluminium concentration. This observation was important because it made possible the direct polarographic determination of an ion most difficult to determine in trace amounts by other methods (sensitivity under optimum conditions for oscillographic polarographic techniques may be in the ppb† range;[2] the sharply peaked waveforms of the dihydroxyazo dye chelates are maintained even at extreme dilution) and because polarographic reductions involving these dyes appear to be the only cases thus far discovered in which the organometallic complex yields a wave distinctly different from that of the organic reagent.[3]

Since the original work of Willard and Dean, other *o,o'*-disubstituted azo dyes have been shown to behave similarly, but selectively, with a number of ions.

The object of this review is to describe the use of these dyes in the polarographic determination of metal ions; to discuss the requirements for polarographic activity both on the part of the dye and of the metal ion; to summarize what is known about the reason for, the mechanism of, and the products arising from, the reduction.

The literature has been examined to December 1966.

DYE CLASSIFICATION AND NOMENCLATURE

Dyes can be classified in a wide variety of ways, *e.g.*, according to the method of preparation or application, according to chemical constitution, or according to the characteristic structural unit. Some 20 different groups of dyes are recognized if classification is by structural unit; the azo dyes constitute the largest class of dyes and are usually considered the group with the fullest shade range and the most diverse uses. The common structural unit is the azo chromophore —N=N— linking two carbon systems at least one of which is aromatic. The azo dyes are further subdivided both according to the number of azo groups the molecule possesses and

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† Parts in 10^9.

according to whether or not the dye reacts with metallic hydroxides and salts to form complexes, *i.e.*, mordants.

Specifically, this review will consider the polarographic behavior of monoazo *o*,*o*′-disubstituted dyes and their respective mordants. The parent structure, shown in Fig. 1 along with structures of the dyes discussed in the paper, contains at least one sulphonic acid group (for solubility) located somewhere in the group; a variety of substituents, quite often other rings, may be attached to any or all of the other positions.

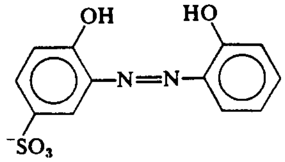
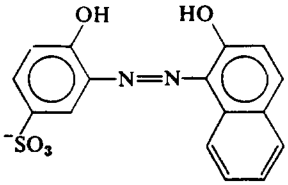
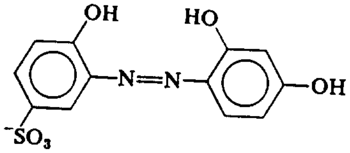
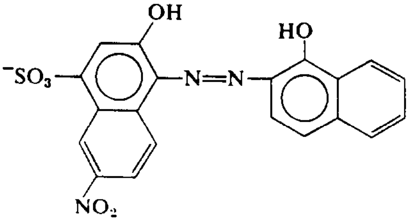
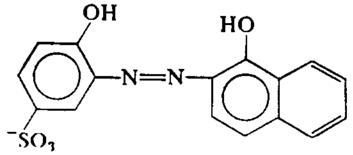
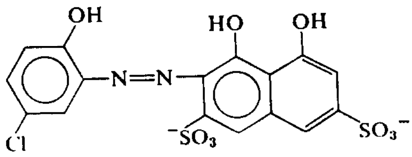
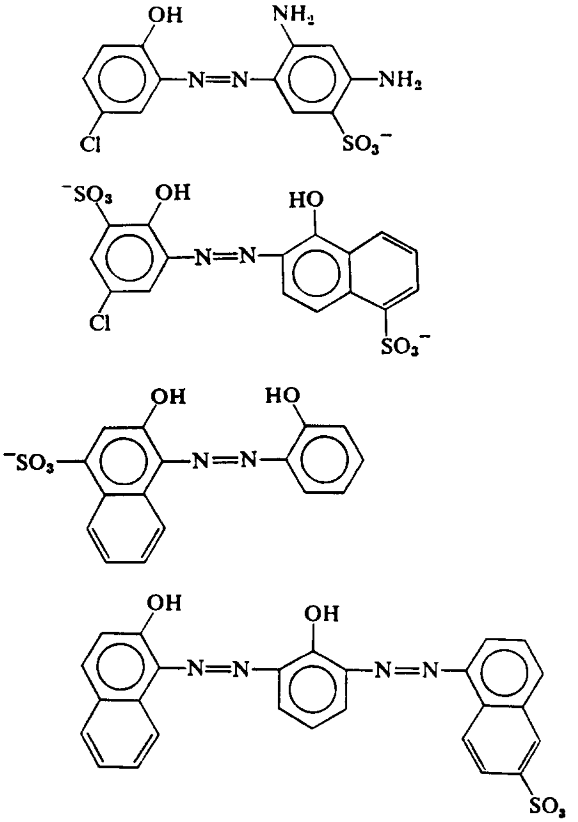
NAME	STRUCTURE	CI NUMBER
Type Compound		———
Mordant Violet 5		15670
Mordant Red 5		14290
Mordant Black 11		14645
Mordant Black 9		16500
Mordant Blue 31		16675

FIG 1



Mordant Brown 33	13250
Mordant Blue 9	14855
Mordant Black 17	15705
Mordant Black 25	21725

Fig. 1.—The structures of mono-azo water-soluble dyes referred in the text.

To minimize confusion when referring to a particular dye, the nomenclature adopted by the *Colour Index* will be used throughout this article. All trade names used by the various investigators have been translated into these terms; in addition, the CI number, which relates the *Colour Index* name to the appropriate section of Part II of the *Index*, is included.

METALS DETERMINED

Aluminium

Mordant Violet 5,[1–10] Mordant Red 5,[2,9] Mordant Black 9,[1,2] Mordant Black 17,[11] and Mordant Black 25[7] all form polarographically reducible complexes with aluminium. The first two dyes are preferred because of their sensitivity and because their solubilities permit the determination of a wider range of concentrations; the upper limit for the determination is set by the dye solubility—a value which changes with the dye lot used.[11] (The problem of dye solubility is discussed in the section "The nature of the dye-metal complex".)

The reaction between aluminium and Mordant Violet 5 has been most widely studied. Two distinct complexes are formed; at pH values between 4·2 and 5 (4·5 is commonly used in most analytical determinations) the dye:Al ratio is 1:2, and at pH 6 the ratio is 1:3 (other investigators have only found 1:1 and 1:3 complexes[12]);

both are polarographically reducible.[6] At room temperature, the complex requires about 5 hr to form, at 50° about 5 min, and at temperatures above 60° about 2 min;[1] no kinetic data have been published. Fluoride, citrate and phosphate interfere by preferentially complexing the aluminium;[11] sulphate, chloride and potassium by precipitating the dye. Metal ions which interfere by forming complexes with $E_{1/2}$ values which overlap that of aluminium are removed by electrolysis at a mercury cathode.[1] Although beryllium does not itself form a polarographically reducible complex with the dye, it does depress the wave height and must be removed.[8] The minimum ratio Be:Al quoted as being necessary to affect the result differs according to investigator.[5,8,9]

The range of aluminium concentrations which can be determined if the polarograms of the Mordant Violet 5 complex are taken in acid solution appears to be 0·001–0·600 mg/ml. In alkaline solutions (pH 9 borate buffer) the range is 0·4–20 μg/ml.[5] The use of alkaline solutions has the advantage that magnesium and aluminium can be determined simultaneously; for the analysis of rocks, however, at pH 4 a larger Be:Al ratio can be tolerated than at a high pH.[5] The Mordant Violet complex has been used to determine aluminium in thorium. The advantage of this procedure is that the thorium forms a non-reducible complex with the dye which is more stable than those of most ions which would normally interfere with the aluminium wave, but less stable than the aluminium complex.[2]

Mordant Red 5 reacts with aluminium over a wider pH range (3·4–5·8) than does Mordant Violet 5.[9] The use of this dye and linear sweep oscillographic polarography permits the determination of as little as 0·1–7·5 μg/25 ml but the concentration of dye must be carefully controlled at about $10^{-4}M$.[2] The pH at which the complex is developed depends on the sample matrix: to determine between 100 and 2000 ppm of aluminium in beryllium, the pH of the solution should be 3·4;[9] for aluminium in thorium, 5·75.[2] Since at room temperature about 5 hr are required for quantitative formation of the complex, the solution is heated to about 70°.

The complex between aluminium and Mordant Black 25 yields three waves,[7] two of which appear to arise from reduction of the complex; this behaviour is analogous to that of the gallium–Mordant Red 5 complex. No quantitative data are available.

Fluoride may be indirectly determined by measuring the depression of the aluminium–Mordant Violet 5 complex.[10] The actual composition of the aluminium–dye solution used depends on the concentration of fluoride expected. As little as 10^{-3} μg/ml or as much as 0·8 μg/ml may be determined, a cathode ray polarograph being used for the lower concentrations. The solutions must stand overnight before polarograms are taken, because of the slow rate of reaction between aluminium and fluoride ions. The procedure has been used to determine fluoride in hydrochloric acid and bromine.

Iron

Iron(III) forms a brownish complex with Mordant Violet 5 at pH values between 4 and 5;[8,11,13] iron(II) does not react. The upper limit of detection is 100 μg/50 ml. The rate of formation of the complex may be hastened by heating the sample for 3 min in boiling water; normally, formation is complete after 15 min. In materials where iron is the major contaminant, *e.g.*, foodstuffs, soft drinks, alcoholic beverages, and effluent streams, no separation is needed. In materials containing indium, aluminium, nickel or silver, or in alloys, the iron is separated either by extraction with ether from 6*M* hydrochloric acid or by extraction of iron cupferronate with an organic solvent; copper, tin, lead, manganese, chromium(III) bismuth, arsenic(III), mercury(II), zinc, antimony, selenium(IV), cerium(IV), thorium, tellurium(IV), germanium, thallium(I) and tungsten do not interfere. Fluoride, phosphate and citrate, which seriously interfere with the formation of the aluminium complex, do not appear to interfere until their concentrations are much larger than that of the iron(III); however, at fluoride to iron ratios of 500 or more a new unstable peak of unknown origin appears.[2]

Magnesium

Between 0·5 and 10 μg/ml can be determined by polarographic reduction of the metal–dye complex which is formed by heating a solution of magnesium with Mordant Violet 5 in a piperidine buffer at pH 11 or 13 (there is no reduction in the pH range 4·5–7·5).[14] Although concentrations of calcium less than 40 μg/ml do not interfere, higher concentrations influence the pH at which a suitable reduction wave can be obtained; large amounts of calcium are therefore removed by precipitation with oxalate, a procedure used to determine as much as 2500 ppm of magnesium in calcium carbonate.[15] Up to 5000 ppm of cadmium, copper, fluorine, lead, thallium(I), tin(II) and zinc can be tolerated as well as about 1000 ppm of antimony(V), arsenic(III), beryllium, bismuth(III), manganese(II), molybdenum(VI) and vanadium(II). Aluminium, although it does not give a wave, chromium, cobalt, iron, nickel and strontium in element to magnesium ratios greater than 25 and barium in ratios greater than 40, all interfere. The interference from iron is best eliminated by extraction of ferric cupferronate. The shape of the wave depends on the piperidine concentration. Although the dye to metal ratio is 1:1, a ratio which appears to hold for aqueous solutions of magnesium and any *o,o'*-disubstituted azo dye,[3,16,17] the dye to metal concentration must be held constant to obtain reproducible results. The half-wave potential for the complex lies between —0·80 and —0·88 V.[5,14]

Reduction of the Mordant Violet 5 magnesium complex can also be effected at pH 9 in borax buffer.[5] Magnesium concentrations between 0·1 and 1 mg/50 ml from complicated mixtures such as rocks can be determined.

Magnesium has also been determined by measuring the decrease in height of the Mordant Black 11 (Eriochrome Black T) reduction wave. Mordant Black 11 in 0·1*M* sodium hydroxide gives two reduction waves, one at —0·63 V and the other at —0·80 V, but the dye–metal complex is not itself reduced.[18]

Gallium

While the range of gallium concentrations which can be determined by direct polarographic reduction of gallium(III) lies between 3×10^{-6} and $3 \times 10^{-5}M$,[19] concentrations as large as $10^{-4}M$ can be determined by reduction of the gallium(III)–Mordant Violet 5 complex. The conditions for formation of the complex are those for aluminium. Gallium can be determined in the presence of aluminium by extracting the gallium from 6–7*M* hydrochloric acid into diethyl ether (the use of di-isopropyl ether leads to badly distorted polarograms); if iron is present it should be reduced to iron(II) with hydroxylamine hydrochloride. The number of electrons required in the reduction of the gallium complex is twice that for the aluminium one.[20]

Mordant Red 5 also forms a polarographically reducible complex with gallium[21] (and with aluminium); however, three waves appear instead of the two expected.

From 10^{-6} to $10^{-3}M$ gallium can be determined by measuring the height of the first wave; slightly greater sensitivity is available through use of the second wave. The complex is formed by heating the gallium(III)–dye solution for 15 min at 70° and pH 5·5 (acetate buffer). As the corresponding aluminium chelate gives only two reduction waves with the dye the two metals may be determined simultaneously by measuring the height of the second wave, which is proportional to the sum of the concentrations, and the height of the third, which is proportional to the concentration of gallium alone; aluminium may be determined by difference. Such a procedure is effective as long as the ratio of aluminium to gallium does not exceed 5. No explanation of the difference in behaviour of these complexes has yet been offered. Zinc, manganese(II), cerium(IV), iron(III), vanadium and nickel interfere.

Lanthanides

Mordant Violet 5, Mordant Black 9 and Mordant Blue 31 all form polarographically reducible complexes with the lanthanides in the presence of either ammonia[22] or piperidine.[14,22]

Of the three dyes Mordant Violet 5 is most satisfactory, giving discrete reduction waves only in alkaline solution. The upper concentration limit of lanthanide is about 6 μg/ml. The reduction waves for the complex are irreversible.

Violet 5 forms a 2:1 dye to metal complex. In ammoniacal solution the difference in $E_{1/2}$ between the waves for the free dye and the lanthanide complex increases with increasing atomic weight; *e.g.*, $\Delta E_{1/2}$ for La is 45 mV while that for Lu is 234 mV. This effect permits simultaneous determination of lighter and heavier lanthanides in a mixture. No such effect is observed in piperidine buffer (pH 11); all $\Delta E_{1/2}$ values are very similar.[22,23]

The $E_{1/2}$ values for the lanthanum and yttrium complexes at pH 13·0 in piperidine are −0·84 and −0·83 V respectively[13] and −0·66 for the dye with respect to a mercury pool anode.

Nickel

Mordant Violet 5 forms a 2:1 dye to metal complex in ammoniacal solution, and a 3:1 complex in the presence of piperidine (pH 13). Both of these, and also one formed between nickel and Mordant Brown 33, are polarographically reducible.[4,8,24] Nickel also forms a complex with Violet 5 at pH 4–5; the wave is, however, not well-defined.[11]

Uranium

Between 2 and 200 mg of uranium can be determined by using Mordant Blue 9, the upper limit being set by the dye solubility (which varies with the ionic strength). The complex is formed by heating the solution (acetate buffer at pH 5·3) for 5 min at 60° since at room temperature complex formation requires 20 min. Triton X-100 is used to suppress the dye maximum. The dye to metal ratio is 1:1. Aluminium, iron, cobalt, nickel, thorium, titanium, vanadium, lead, copper and zirconium interfere.

The sodium salts of (1,5-sulpho-2-hydroxyazo)-2-naphthol and chlorophenol-azo-1,8-dihydroxynaphthalene-3,6-disulphonic acid give well-defined waves with uranyl ion but the wave height is not proportional to the concentration of uranium.

Zirconium

Mordant Blue 9 can be used to determine 40–300 μg of zirconium. The complex is developed by heating at 70° for 5 min. The dye to metal ratio is 2:1.[25] Mordant Violet 5 also forms a complex; at a pH between 2 and 3, which has been used for determination of zirconium in thorium, the latter being masked with acetate.[26]

Chromium

Chromium(III) forms complexes with *o,o′*-dihydroxy,*o′*-carboxy, and *o*-hydroxy-*o′*-amino dyes. The organic ligand behaves as a tridentate ligand with one azo group acting as donor.[27] With six co-ordinate positions, both 2:1 and 1:1 dye to metal complexes are possible; in the case of chromium(III) and Violet 5 both have been found, and separated by chromatography on cellulose.[27] The 2:1 complex is itself not chromatographically homogeneous.[12] Both the 1:1 and 2:1 Mordant Violet 5 complexes show the characteristic pair of waves, one for the dye and one for the complex, but the complexes are polarographically indistinguishable.[12]

Other metals

As Table I shows, a number of other elements give similar reactions with one or more dyes. In these cases analytical details have not been worked out specifically either because other more satisfactory polarographic methods exist or because there is no present demand for such a method.

TABLE I.—ELEMENTS FORMING POLAROGRAPHICALLY REDUCIBLE COMPLEXES WITH MORDANT VIOLET 5

Element	Reference	Element	Reference
Al, Fe(III), Mg, Ga Lanthanides Ni, U, Zr, Cr	See text	Co Ti(IV) V(V)	8, 11, 12 1, 3, 5, 8, 12 1, 3, 8, 11, 12
Mn(II)	3, 14	Pb	8
Mo	8	Zn	3, 14
Pb(V)	8	Cd	3, 8
Sb	8	In	11

Evaluation of the published methods

Of the procedures discussed above, those for aluminium, gallium, zirconium and lanthanides appear the most useful, competing with spectrophotometric methods both in applicability and sensitivity for trace analysis.

THE NATURE OF THE DYE–METAL CHELATE

Present evidence indicates that only *o,o′*-disubstituted dyes undergo reactions which will produce complexes which have $E_{1/2}$ values different from that of the organic compound.[3,13] Two reasons are suggested.

1. The metal may not be incorporated into an appropriate ring system or it may not react with the dye at all. Disubstituted dyes form a wider range of lakes and complexes than do monosubstituted dyes, *e.g.*, iron(III), magnesium, chromium(III), zinc, calcium and manganese(II), do not react with monosubstituted dyes; aluminium does not form a lake with the monosubstituted dye,[28] but forms instead a Werner

complex.[13] Other substituents on the dye may change its complexing behaviour: although the presence of a sulphonic acid group may not be of immediate importance in determining whether a dye forms a metallo-organic indicator,[17] its presence or absence can affect the formation of a complex as well as the ratio of metal to dye, *e.g.*, copper does not form a lake with *o*-monohydroxy dyes if an aromatic sulphonic acid group is present and, if two sulphonic acid groups are available in a dihydroxy dye, it forms a complex containing a 2:1 Cu:dye ratio rather than a 1:1.[28]

2. The complex between a monosubstituted dye and a metal ion simply may not be stable enough to show a shift in $E_{1/2}$.[13] The relative order of co-ordination with a metal such as copper is shown in Fig. 2.[29]

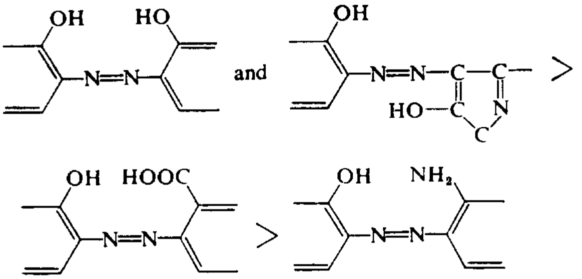


FIG. 2.—Relative order of co-ordination of *o,o'*-disubstituted azo compounds with a given metal.

Within the disubstituted dye series, the dihydroxy compounds appear to be most useful for developing this polarographic behaviour (no comparisons, however, have actually been made.) As Fig. 2 shows, complexes involving the dihydroxy groups are by far the most stable. Specifically, the *o*-hydroxy-*o'*-carboxyl dye–metal complexes have formation constants two orders of magnitude less than those of the corresponding dihydroxy complexes,[16] which might be expected since the stability of a complex is inversely proportional to the pK_a values of the *o,o'*-substituents.[29,30] Some exceptions, however, exist: beryllium does not form polarographically reducible compounds with dihydroxy dyes (although it does form a fluorescent chelate[31] and a lake[32]). *o*-Hydroxy-*o'*-carboxy azo dyes form compounds with beryllium which have not been investigated but might prove to be polarographically active because in this case the phenolic and carboxylic hydroxyl can get close enough together to bond the beryllium in a stable ring.[30] Stability constants have been determined for a number of the complexes,[30] and for any one dihydroxy dye the order of stability appears to be, in the case of bivalent ions, $Cu^{2+} > Ni^{2+} > Zn^{2+} > Pb^{2+} > Cd^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ and for tervalent ions, $Fe^{3+} > Cr^{3+} > Al^{3+}$.

The valence and the nature of the ion involved in the reaction obviously play a significant role. In general, tervalent ions show the greatest tendency to form complexes while higher valences show less, *i.e.*, antimony(III) reacts more readily with Violet 5 than does antimony(V).[8]

A specific study of Mordant Violet 5 complexes with aluminium, nickel, zinc, lead, magnesium and calcium shows evidence for 1:1 and 1:2 metal to dye ratios; aluminium has been reported to form a 1:3 complex, but copper shows evidence of only a 1:1 complex.[12]

Many dyes which fulfil the structural requirements are too insoluble for use. Consideration of solubility, then, must also be a factor in the selection of a dye since solubility places a limit on the range of concentrations which can be determined polarographically. Since the solubility of the dye changes with the batch, the upper concentration limit for the determination of a metal ion has always been determined empirically. No attempt has, as yet, been made to extend the range of applicability by introducing more solubilizing groups into the molecule.

Neither dye solubility nor formation of a complex with a dihydroxy dye, however, implies that the complex is *a priori* reducible. Calcium clearly reacts with Mordant Violet 5 in the pH range 3·9–13; so far no shift in $E_{1/2}$ for the complex has been observed.[14] Although Eriochrome Black T is polarographically reducible and forms a complex with magnesium, the complex does not appear to be reduced at a potential different from that of the dye itself;[18] the same is true for Mordant Brown 33 and its nickel complex.[24]

In formation of the complex, both phenolic hydrogen ions are displaced[27] and the azo group is apparently bonded to the metal, stabilized by resonance.[12,23,33] The structure is probably a strain-free five-membered ring (Fig. 3).[7,34] The reaction is slow in acid, becoming faster with increase in temperature, but immediate in base;[4] no kinetic data have yet been published. Foreign ions can decrease the rate of reaction between the dye and the reacting metal ions.[2]

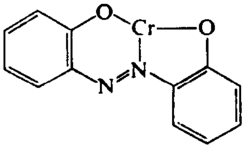


FIG. 3.—Proposed structure for the chromium–dye complex.

Even in dyes symmetrical except for the present of a sulphonic acid group, it does not appear that the two hydroxy groups are equivalent. Schetty has shown[35] that those dyes where the sulphonic acid group is *ortho* or *peri* to the hydroxyl group have special physical, chemical, and mordant characteristics, but information about other characteristics of the two hydroxyl groups is scant: the pK_a values for the ionization of the phenolic hydroxyl groups as well as their enthalpies and entropies of ionization have been determined for Mordant Violet 5.[36]

A number of suggestions have been made concerning the structure of specific metal–dye chelates: Reynolds suggests that the aluminium complex formed at pH 4·6 contains a fused ring structure in which the *o*-hydroxy group linkages in the *trans* dye molecule are as nearly *cis* and coplanar as is permitted by the metal bonding, but no such simple structure can be used to explain the aluminium–dye complex formed at pH 6·5.[13] In chromium(III)–dye complexes (either 1:1 or 2:1) there is no change in the chromophoric system so that they probably retain the *trans* configuration around the azo nitrogen double bond[27]—a proposed structure is given in Fig. 3.[34]

Beech and Drew[28] have suggested a general structure for dye complexes which may or may not be applicable in these systems, but is consistent with the evidence gathered for fluorescence phenomena[31] for which the requirements for activity are strikingly similar to those for polarographic activity.

Polarographic reduction products

Since reduction of the dye–metal complex takes place at the azo linkage, the mechanism is believed similar to that for azobenzene.[5,6] Though the reduction of substituted azobenzenes is not simple, numerous conflicting statements appear,[37] and the extension of specific findings to general behaviour is risky, the following conclusions seem reasonable.

1. If the dye contains no other reducible groups, the reduction at the azo linkage proceeds in stages.[24]

$$\text{—N=N—} + 2H^+ + 2e^- \longrightarrow \text{—NH—NH—} \qquad A$$

$$\text{—N=N—} + 4H^+ + 4e^- \longrightarrow 2(\text{—NH}_2) \qquad B$$

2. Both the type and position of substituents greatly affect the ease of reduction. *p*-Substituted sulpho-, carboxy-, or phenylamino-azobenzenes are more easily reducible than the parent compound,[38] but *o*-hydroxyazo dyes are reduced at values some 100 mV more negative than the corresponding *para* compounds.[39] According to Shikata and Tachi, electron-releasing ring substituents increase resistance to reduction.[39] However, studies have shown that while $E_{1/2}$ values for different dyes vary, the differences are not large and do not appear to bear any simple relation to important features of molecular structure.[24]

3. The nature of the group also affects the reduction path. Only when strongly releasing groups are present does the electrode reduction involve more than 2 electrons.[40] *o*-Hydroxy substituted azobenzenes give a 4*e* reduction at all pH values; *p*-sulphonic acid substituted azobenzenes require but 2*e*, proceeding only to the hydrazo state.[41]

Since azo dyes may contain a number of different substituents, various effects compete and investigation has shown that while some dyes are reduced only to the hydrazo state, others cleave and form amines. Florence suggests that the apparently differing reduction paths can be explained by assuming that the rate of disproportionation of the hydrazo intermediate decreases with increasing pH and becomes sufficiently slow to give an apparent peak height corresponding to 2*e*. Disproportionation appears first-order with respect to [H$^+$] and pseudo first-order with respect to hydrazo concentration.[40] Studies of the reduction of Mordant Violet 5 suggest that such a mechanism is involved.

4. The reversibility of the reduction is apparently pH-dependent, azo dyes being reversibly reduced in alkali,[42] but Mordant Violet 5 is not reversibly reduced in acid.[6] Examination of a simple type-compound, azobenzene-4-sulphonic acid, shows it is reduced reversibly at high and low pH but irreversibly at intermediate values.[41]

Over the years considerable evidence has accumulated indicating that both *o*-hydroxyazo and *o,o'*-dihydroxy azo groups are internally hydrogen bonded; the suggested configuration for the dye is that shown in Fig. 2.[37,43,44] The strength of this internal hydrogen bond affects the ease of reduction of the compound.[39]

Another factor which has not yet been treated is the effect which dimerization of the dye has on the polarographic characteristics of the complex. It should be significant since dimerization affects the pK_a values.[45] At concentrations above $10^{-5}M$, the dye is known to exist as shown in Fig. 4,[45] the dimer produced in acid solution giving maximum overlap.[12] There is little likelihood of intramolecular hydrogen-bonding.

While aggregation is known to affect the pK_a values for both the phenolic groups as well as the stability constants, the studies made have not taken this into account.[45]

Purity of the dye

Commercial dyes must be purified before use. A common practice is to recrystallize the dye from ethanol (pH 5) and dry over silica gel.[22] The process is repeated until no changes are observed in the dye's spectrophotometric or polarographic characteristics.

Others have determined the purity of their dyes either by the amalgam reduction–EDTA titration proposed by Scribner and Reilley[46] or the titanium(III) reduction procedure of Knecht and Hibbert.[27,47]

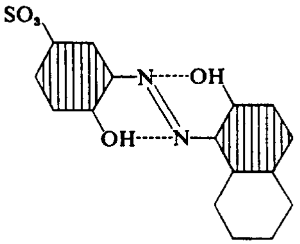


FIG. 4.—Proposed structure for dimer of hydroxyazo dyes (shaded area indicates the overlapping of the two rings; the two SO_3^- groups are as far apart as possible).

A more elaborate procedure described by Robinson and Mills[48] involves repeated salting-out of the dye until the test for chloride is negative; the dye is then boiled in alcohol, filtered, and washed. A critical examination of this procedure by Coates and Riggs[36] has shown that for many dihydroxyazo dyes it cannot be directly adapted for the purification because the product obtained contains substantial amounts of the disodium salt of the dye. To avoid this contamination, they found it necessary to buffer the salting-out solution at a pH about three units below the pK_a for the first hydroxyl group (for Mordant Violet 5, a pH of 4 proved satisfactory); the most convenient salting-out agent was a sodium acetate–acetic acid buffer. The purity of the product was determined in two ways: by potentiometric or conductometric titration of the 2′-hydroxy group with base and by titration with nitric acid.

The importance of the dye purity cannot be overemphasized.[36] Failure to use pure compounds has put into question results for the metal:dye ratio[17] as well as the number of electrons involved in the reduction.[22]

Two additional precautions should be taken: (*a*) the dyes are hygroscopic and suitable precautions should be taken to protect them; (*b*) many of the "inert" salts added, *e.g.*, those used to maintain constant ionic strength, contain traces of elements which will complex the with dye. Coates and Riggs suggest the use of EDTA as a masking agent.[36]

EXPLANATIONS OF POLAROGRAPHIC ACTIVITY

What is the reason for the splitting of the polarographic wave if the site of reduction is the azo linkage? Willard and Dean[1] have suggested that the appearance of the two waves is caused by stabilization of one of the possible geometrical isomers of the dye (which form was not specified) and that it is this form of the complex which is being reduced. Despite Dean's later suggestions[3] that the chelate involves the stabilization of a rigid *cis* form, theoretical considerations (a concise summary of these arguments is given by Perkins and Reynolds[7]) and accumulated physical evidence suggest that the *o*-hydroxy groups prevent the dye molecule from ever assuming the *cis* configuration.[7,9,14,44]

Experiments have demonstrated that the $E_{1/2}$ values of *p*-hydroxyazo dyes are 100 mV more positive than those of the corresponding azo dyes.[39] Meche and Schmal suggest that this observed stabilizing effect of the *o*-hydroxy group is caused by internal hydrogen bond formation.[39] A second explanation for the observed difference between the $E_{1/2}$ values for the dye and for the dye–metal chelate would be that in the latter the dye is not hydrogen-bonded. Unfortunately, the observed effect appears in the opposite direction, *i.e.*, the dye–metal should give a reduction wave at more positive potentials since they should be more easily reduced. It is, of course, possible that this effect competes with stabilization of the nitrogen electrons in the ring—the azo group is involved in the complex formation and this alone might account for the difference in $E_{1/2}$ values[24]—and that the overall effect is to move the $E_{1/2}$ to more negative potentials. If differences in stabilization of the nitrogen electrons account for the shift, there should be differences in the $E_{1/2}$ values of the various complexes of the same dye, depending on the element involved. Present evidence is contradictory: such a trend is suggested by the change of half-wave potential with atomic number for the lanthanide complexes in ammoniacal solution,[21,22] but apparently not with other elements nor even with the lanthanide complexes in the presence of piperidine.

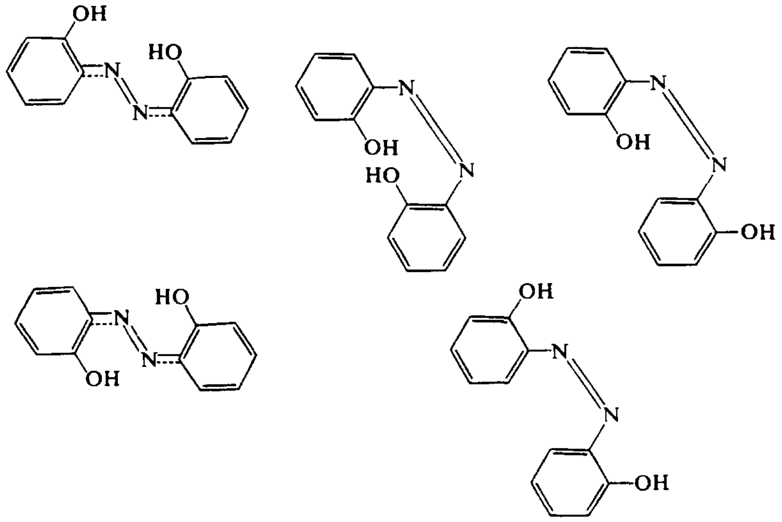


Fig. 5.—Possible geometrical isomers of *o*,*o*′-dihydroxyazo dyes.

Theoretically there are five possible isomers of the dihydroxy azo dyes (see Fig. 5). In addition to the *cis* forms, two isomers of the *trans* dye can exist since rotation is restricted around the —C—N= bond. Since the aluminium complex with Mordant Violet 5 is believed to be *trans* but as nearly *cis* as possible,[13] it may exist in the *trans-anti* form. The energy differences involved between these two states could explain the differences in $E_{1/2}$.

Although the behaviour of both the dye and the metal complex are known to be greatly influenced by adsorption at the mercury interface[23] and although adsorption-desorption is believed to be the reason for the increased sensitivity obtained by oscillographic polarography,[22] apparently no investigation has been made of the possibility that such a phenomenon is responsible for the appearance of the discrete polarographic waves.

The available data, however, are at present too scattered and lack the systemization which would suggest whether the answer to the question lies in any of the above suggestions or in an entirely new area.

OXIDATION OF DYE METAL CHELATES

Although the foregoing review has concentrated on polarographic reduction, polarographic oxidation studies have been made of the aluminium–Mordant Violet 5–complex. Florence, Miller, and Zittel have shown that at a pyrolitic graphite electrode this complex shows an oxidation wave well separated from that of the dye (~0·35 V).[49] The use of the oxidation step has the following advantages: (1) sensitivity (~10 ppb) even with simple polarographic equipment; (2) the test solution need not be deaerated; (3) the interference of other metals is minimized.

Presumably such techniques can be adapted in a direct manner to other dye–metal systems.

Zusammenfassung—Die Natur der Komplexe aus verschiedenen *o, o'*-Dihydroxyazofarbstoffen und Metallionen und deren Anwendugen in der polarographischen chemischen Analyse werden beschrieben und diskutiert.

Résumé—On décrit la nature des complexes entre divers colorants *o, o'*-dihydroxyazo et les ions métalliques, et leurs applications en analyse chimique polarographique, et en discute.

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ELEKTRONISCHES RECHNEN IN DER ANALYTISCHEN CHEMIE—IV*

ALGOL-PROZEDUR FÜR AUSGLEICHSFUNKTIONEN MIT ZWEI KONSTANTEN

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Zusammenfassung—Optimale Funktionen zur mathematischen Beschreibung eines Zusammenhanges zwischen verschiedenen Reihen von Merkmalsgrößen, die an gleichartigen Objekten oder Vorgängen gemessen wurden, können durch Ausgleichsrechnungen für eine Folge systematisch variierter Ausgleichsfunktionen aufgefunden werden. Hierzu wird im folgenden die mathematische Struktur einer UNIVERSELL verwendbaren Ausgleichsfunktion mit 2 Konstanten, einschließlich der in ihr enthaltenen 2 reduzierten Funktionen mit jeweils nur 1 Konstanten, entwickelt und als Prozedur AUSGL2 (Unterprogramm) in der problemorientierten Sprache ALGOL für eine elektronische Datenverarbeitung formuliert. Die Prozedur AUSGL2 ist ein kybernetischer SCHWARZER KASTEN, der als geschlossener Baustein in ein zumeist sehr einfaches Rahmenprogramm für spezielle Problemstellungen eingesetzt wird und dessen praktischer Gebrauch nur geringe mathematische Kenntnisse voraussetzt. An kurz skizzierten Beispielen des Funktionseinsatzes zum bivalenten, trivalenten und polyvalenten Ausgleich von entsprechenden Reihen analytischer Merkmalsgrößen werden teilweise neuartige Wege einer rationellen Versuchs- und Auswertetechnik aufgezeigt. In einem abschließenden ausführlichen Beispiel werden 2 flammenphotometrische Testreihen für Na und K in Konzentrationsbereichen funktionell aufgeschlüsselt, wo durch Effekte der Selbstabsorption und Selbstumkehr bereits gekrümmte Eichkurven resultieren. Über ein einfaches Rahmenprogramm werden insgesamt 8 (2 mal 4) Funktionen in weniger als 17 min elektronisch ausgewertet, während der Zeitbedarf bei konventioneller Rechentechnik mehr als 170-fach größer ist.

WESENTLICHE VERWENDETE BEGRIFFE UND SYMBOLE (ALGOL-SYMBOLE IN KLAMMERN)

Gesamtanzahl paralleler Meßdaten	n	(N)
Laufzahl für Einzelgrößen		(I)
Formale Parameter der Ausgleichsfunktion	$Y, Z1, Z2$	(Y, Z1, Z2)
Konstanten der Ausgleichsfunktion	[A], [B]	(A, B)
Standardabweichung in Y-Einheiten	[s_K]	(SK)
Fehler der Konstanten	[s_A], [s_B]	(SA, SB)
t-Werte der t-Verteilung	t_1, t_2, t_3, t_4	(T1, T2, T3, T4)
Boole'sche Variable	$V1, V2$	(V1, V2)

Weitere Größen sind im Text eindeutig definiert.

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* Teil III—*Talanta*, 1967, **14**, 1315.

EINFÜHRUNG

Allgemeine Problemstellung

Der optimale funktionelle Zusammenhang zwischen abhängigen Variablen y und unabhängigen Variablen x

$$y = \mathrm{F}(x) \text{ oder } y = \mathrm{F}\{x(1), x(2), \ldots, x(J), \ldots\} \tag{1}$$

bei jeweils n parallel ermittelter Merkmalsgrößen

$$y_i, x_i \text{ bzw. } y_i, x(1)_i, x(2)_i, \ldots, x(J)_i, \ldots$$

für gleichartige Objekte oder Vorgänge kann über AUSGLEICHSRECHNUNGEN mit verschiedenen vorgegebenen Ausgleichfunktionen gefunden werden. Die Durchführung von Ausgleichsrechnungen ist naturgemäß nur dann sinnvoll, wenn von vornherein ein Zusammenhang zwischen den Merkmalsgrößen als sicher vorausgesetzt werden kann. In Zweifelsfällen sollten vorerst Korrelationsrechnungen durchgeführt werden, wie sie in Arbeit III ausführlicher beschrieben wurden, zumal geeignete Korrelationsfunktionen wertvolle Hinweise für optimal erscheinende Ausgleichsansätze liefern.

Unter der Vielzahl denkbarer Ausgleichsfunktionen wird im folgenden eine UNIVERSELLE FUNKTION MIT 2 KONSTANTEN [A] und [B] der Form

$$Y = [\mathrm{A}] \cdot Z1 + [\mathrm{B}] \cdot Z2 \tag{2}$$

mathematisch aufgeschlüsselt und praktisch angewendet. Die Größen Y, $Z1$ und $Z2$ symbolisieren FORMALE Parameter, die stellvertretend für ARITHMETISCHE AUSDRÜCKE stehen. Diese Ausdrücke sind Rechenvorschriften, die mit den eindimensionalen Datenfeldern der Merkmalsgrößen (Laufzahl $i = 1, 2, \ldots, n$) und eventuell anderen numerisch vorher bekannten Einzelgrößen gebildet werden. Tabelle I bringt 5 Beispiele von wählbaren Funktionen und Parameter, die die große Variationsbreite des Ansatzes (2) verdeutlichen.

Ziel der Ausgleichsrechnung ist die Ermittlung der 5 Kenngrößen

$$[\mathrm{A}], [\mathrm{B}] = \text{Konstanten der Ausgleichsfunktion}$$
$$[s_{\mathrm{K}}] = \text{Standardabweichung in } Y\text{-Einheiten}$$
$$[s_{\mathrm{A}}], [s_{\mathrm{B}}] = \text{„mittlerer" Fehler von [A] bzw. [B]}$$

Tabelle I.—Beispiele aktueller Ausgleichsfunktionen zum formalen Ansatz (2)

	Funktion	Parameter		
		Y	$Z1$	$Z2$
(I)	$y = [\mathrm{A}] + [\mathrm{B}] \cdot \log x$	y_i	1	$\log x_i$
(II)	$y = [\mathrm{A}] \cdot x + [\mathrm{B}] \cdot x^2$	y_i	x_i	x_i^2
(III)	$y = a \cdot e^{b\cdot}$ (siehe Anm.)	$\ln y_i$	1	x_i
(IV)	$y = [\mathrm{A}] \cdot x(1) + [\mathrm{B}] \cdot x(2)$	y_i	$x(1)_i$	$x(2)_i$
(V)	$y = [\mathrm{A}]\{x(1) - x(2)\} + [\mathrm{B}] \cdot \frac{x(3)}{x(4)}$	y_i	$x(1)_i - x(2)_i$	$\frac{x(3)_i}{x(4)_i}$

Anmerkung: Bei der Funktion (III) ist weiterhin $[\mathrm{A}] = \ln a$ bzw. $a = e^{[\mathrm{A}]}$ und $[\mathrm{B}] = b$

für eine bestimmte, jeweils vorgegebene Ausgleichsfunktion, wie sie Tab. I in 5 Beispielen zeigt. Der Begriff „AUSGLEICH" definiert eine Ermittlung der Konstanten [A] und [B] in einer solchen numerischen Größe, daß die Quadratsumme der Abstände v_i in Y-Einheiten der gefundenen Meßpunkte von der theoretischen Punktfolge der Ausgleichsfunktion ein Minimum wird. Diese GAUSS'SCHE MINIMUMS-BEDINGUNG, die bereits in Arbeit III (Korrelationsrechnung) verwendet wurde, hat speziell für (2) die Form:

$$\sum_1^n v_i^2 = \sum_1^n \{[\mathrm{A}] \cdot Z1 + [\mathrm{B}] \cdot Z2 - Y\}^2 = (n-2) \cdot [s_\mathrm{K}]^2 = \mathrm{MINIMUM} \qquad (3)$$

Unter einer Reihe vorgegebener Ausgleichsfunktionen zeichnet sich die OPTIMALE Funktion zunächst durch

möglichst einfache Funktionsteile Y, $Z1$, $Z2$ und durch eine
möglichst kleine Standardabweichung $[s_\mathrm{K}]$

aus. Die Aufstellung einer Reihe von Ausgleichsfunktionen kann zwar rein empirisch nach den Kurvenformen graphischer Darstellungen des aktuellen Datenmaterials erfolgen, doch ist es dabei zweckmäßig, bereits bekannte oder neu erdachte Hypothesen und vermutete Mechanismen bei der Formulierung der Funktionsteile zu berücksichtigen.

Die Ausgleichsrechnung für eine aktuelle Funktion des Typs (2) kann für die Konstanten [A] oder [B] oder für beide auch numerische Werte ergeben, die sich unter Berücksichtigung der Fehler $[s_\mathrm{A}]$ bzw. $[s_\mathrm{B}]$ nicht signifikant von Null unterscheiden. In diesem Fall sollten Folge-Ausgleichsrechnungen für REDUZIERTE Funktionen des FORMALEN Typs

$$Y = [\mathrm{A}] \cdot Z1 \quad \text{und} \quad Y = [\mathrm{B}] \cdot Z2 \qquad (4)$$

durchgeführt werden. Der mögliche Übergang von (2) auf (4) bedeutet im Rahmen des betreffenden aktuellen Ansatzes vom Typ (2) eine funktionelle Optimalisierung. Für die reduzierten Funktionen vereinfacht sich auch der Minimumsansatz (3) zu:

$$\sum_1^n \{[\mathrm{A}] \cdot Z1 - Y\}^2 = (n-1) \cdot [s_\mathrm{K}]^2 = \mathrm{MINIMUM}$$

bzw. (5)

$$\sum_1^n \{[\mathrm{B}] \cdot Z2 - Y\}^2 = (n-1) \cdot [s_\mathrm{K}]^2 = \mathrm{MINIMUM}$$

Bivalenter Ausgleich

Die Beispiele (I), (II) und (III) der Tab. I beschreiben einen BIVALENTEN Ausgleich, d.h. einen Ausgleich für 2 Reihen paralleler Merkmalsgrößen $\{x_i, y_i\}$. Die jeweilige Ausgleichsfunktion ist eine Kurve in einem X, Y-Koordinatensystem mit minimierten Vertikalabständen v_i der n Parameterpunkte Y_i, X_i. Bei Anwendungen in der analytischen Chemie entspricht y zumeist einer Menge a oder Konzentration C und x einer analytischen Meßgröße.

So sind z.B. bei photometrischen Analysenverfahren Zusammenhänge der Form

$$C = [\mathrm{A}] + [\mathrm{B}] \cdot \log D \quad \text{mit} \quad Y = C_i;\ Z1 = 1;\ Z2 = \log D_i$$

oder (6)

$$C = [\mathrm{A}] \cdot E + [\mathrm{B}] \cdot E^2 \quad \text{mit} \quad Y = C_i;\ Z1 = E_i;\ Z2 = E_i^2$$

zu erwarten. Die 1. Funktion verknüpft C mit der Durchlässigkeit (transmittance) D in %. Bei Erfüllung des Lambert-Beer'schen Gesetzes

$$E = [\varepsilon] \cdot d \cdot C = 2 - \log D$$

sollte wegen $[A] = 2/([\varepsilon] \cdot d)$ und $[B] = 1/([\varepsilon] \cdot d)$ ein Konstantenverhältnis von $[A]/[B] = 2$ erhalten werden. Signifikante Abweichungen von 2 bedeuten eine Nichterfüllung des Idealgesetzes. Die 2. Funktion beschreibt gekrümmte Eichkurven, in denen C als Funktion der Extinktion E dargestellt ist. Bei Erfüllung des Idealgesetzes sollte [B] als nicht signifikant von Null verschieden gefunden werden, während $[A] = 1/([\varepsilon] \cdot d)$ eine ideale Verfahrenskonstante aus Extinktionskoeffizient $[\varepsilon]$ und Küvetten-Schichtdicke d definiert.

Als weiteres Anwendungsbeispiel seien Potentialwert-Messungen $\mathscr{E}$ von Systemen gegen eine Normalwasserstoff-Elektrode (Vergleichspotential Null) genannt. Aus dem theoretischen Nernst-Ansatz

$$\mathscr{E} = \mathscr{E}_0 + \frac{RT}{z \cdot F} \cdot \ln C \quad \text{bzw.} \quad C = \mathrm{EXP}\left\{(\mathscr{E} - \mathscr{E}_0) \cdot \frac{z \cdot F}{RT}\right\}$$

folgt die bivalente Ausgleichsfunktion

$$\ln C = -\frac{z \cdot F}{RT} \cdot \mathscr{E}_0 + \frac{z \cdot F}{RT} \cdot \mathscr{E} \quad \text{mit} \quad Y = \ln C_i; \; Z1 = 1; \; Z2 = \mathscr{E}_i \qquad (7)$$

Wegen $[A] = -z \cdot F \cdot \mathscr{E}_0/(RT)$ und $[B] = z \cdot F/(RT)$ ergeben sich das Nullpotential $\mathscr{E}_0$ aus dem Konstantenverhältnis

$$\mathscr{E}_0 = -[A]/[B]$$

und die Elektronen-Umsatzzahl z unmittelbar aus [B] zu

$$z = \frac{RT}{F} \cdot [B]$$

Die Temperatur T in °K muß während der Durchführung der Versuche konstant gehalten werden, so daß die aus T, Gaskonstante R und Faraday-Konstante F gebildete Größe RT/F insgesamt eine Versuchskonstante definiert.

Trivalenter Ausgleich

Die Funktion (IV) der Tab. I beschreibt einen TRIVALENTEN Ausgleich, d.h. einen Ausgleich für 3 Reihen paralleler Merkmalsgrößen $\{y_i, x(1)_i, x(2)_i\}$. Die jeweilige Ausgleichsfunktion ist im allgemeinen eine Fläche in einem X, Y, Z-Raumkoordinatensystem mit minimierten Abständen v_i der n Parameterpunkte Y_i, $X(1)_i$, $X(2)_i$. Besteht zwischen den Funktionen $X(1)$ und $X(2)$ ein einfacher Zusammenhang etwa der Form $X(2) = K \cdot X(1)$, so bedeutet das eine „verbotene" Zuordnung $Z1 = Z2$ und der entsprechende Funktionsansatz des Typs (2) ist nicht auswertbar.

Der trivalente Ausgleich ist bisher in der analytischen Chemie kaum angewendet worden. Wie das nachfolgend skizzierte Beispiel einer photometrischen Simultanbestimmung von 2 verschiedenen Elementen zeigt, eröffnen sich mit der ZEITSYNCHRONEN Ermittlung von PARALLEL-INFORMATIONEN an EINEM System eine Vielzahl neuer rationeller Arbeitstechniken.

Unter der Voraussetzung, daß das Lambert-Beer'sche Gesetz für beide Elemente 1 und 2 bei beiden Meß-Wellenlängen $\lambda 1$ und $\lambda 2$ erfüllt wird, ist das System durch folgende Informationsgrößen vollständig beschreibbar:

Element	Menge	$\lambda 1$	$\lambda 2$
1	$C1$	$[\varepsilon_{11}]$	$[\varepsilon_{21}]$
2	$C2$	$[\varepsilon_{12}]$	$[\varepsilon_{22}]$
Küvetten-Schichtdicke		$d1$	$d2$
Summen-Extinktion		$E1$	$E2$

Aus den Grundbeziehungen

$$\text{für } \lambda 1\text{: } E1 = [\varepsilon_{11}] \cdot d1 \cdot C1 + [\varepsilon_{12}] \cdot d1 \cdot C2$$

$$\text{für } \lambda 2\text{: } E2 = [\varepsilon_{21}] \cdot d2 \cdot C1 + [\varepsilon_{22}] \cdot d2 \cdot C2$$

folgen unmittelbar die trivalenten Konzentrationsformeln

$$\begin{aligned} C1 &= [A1] \cdot E1 + [B1] \cdot E2 \quad \text{mit} \quad Y = C1_i;\ Z1 = E1_i;\ Z2 = E2_i \\ C2 &= [A2] \cdot E1 + [B2] \cdot E2 \quad \text{mit} \quad Y = C2_i;\ Z1 = E1_i;\ Z2 = E2_i \end{aligned} \tag{8}$$

Die Konstanten enthalten die Koeffizientendifferenz

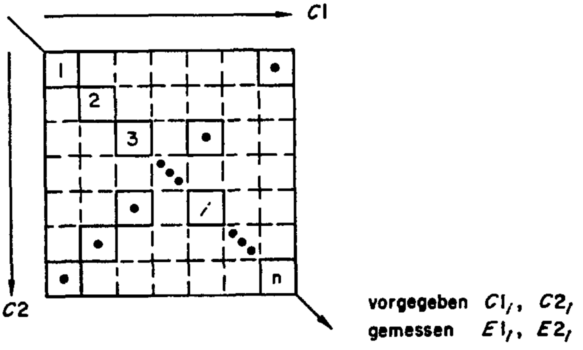
$$\Delta\varepsilon = [\varepsilon_{11}] \cdot [\varepsilon_{22}] - [\varepsilon_{12}] \cdot [\varepsilon_{21}]$$

und ergeben sich formal zu:

$$[A1] = [\varepsilon_{22}]/(d1 \cdot \Delta\varepsilon) \quad \text{und} \quad [B1] = -[\varepsilon_{12}]/(d2 \cdot \Delta\varepsilon)$$

$$[A2] = -[\varepsilon_{21}]/(d1 \cdot \Delta\varepsilon) \quad \text{und} \quad [B2] = [\varepsilon_{11}]/(d2 \cdot \Delta\varepsilon)$$

Man erkennt unmittelbar, daß derartige Simultan-Verfahren nur für $\Delta\varepsilon > 0$, d.h. für hinreichend unterschiedliche Extinktionskoeffizienten $[\varepsilon]$ bei den Wellenlängen $\lambda 1$ und $\lambda 2$, zu Lösungen führen wird. Kennt man von den reagenzmäßig gleichartig zusammengestzten reinen Lösungen der Elemente 1 und 2 lediglich die Tatsache, daß sie farbverschieden sind, so kann man in einer EINZIGEN DIAGONAL-MESSREIHE mit monochromatischem Komplementär-Licht $\lambda 1$ bzw. $\lambda 2$ zu den visuellen Farben feststellen, ob sich weitergehende Untersuchungen überhaupt lohnen. Hierzu werden aus dem Konzentrationsfeld $C1/C2$ n verschiedene Mischungsansätze von $C1$ und $C2$ vorgegeben und die Summenwerte $E1$ und $E2$ gemessen, was nachfolgende Skizze verdeutlichen soll. Danach liefert die doppelte bivalente



Ausgleichsrechnung mit den Konstanten und den Standardabweichungen für $C1$ und $C2$ die benötigten Informationen für die weitere Versuchsplanung. Erhält man reduzierte Funktionen, so liegt der sehr erwünschte Sonderfall vor, daß das Begleitele ment bei der betreffenden Wellenlänge nur vernachlässigbar absorbiert ($[\varepsilon\,..] = 0$!). Werden in weiteren Versuchen die 4 Extinktionskoeffizienten bestimmt, so läßt sich die Voraussetzung der Erfüllung des Idealgesetzes unmittelbar an den Nullbedingungen

$$[A1] \cdot [\varepsilon_{21}] + [A2] \cdot [\varepsilon_{22}] = 0$$

$$[B1] \cdot [\varepsilon_{11}] + [B2] \cdot [\varepsilon_{12}] = 0$$

prüfen, die sich aus den Konstantenformeln ergeben. In einem nächsten Versuchsschritt könnten Meßreihen in der 2. Hauptdiagonalen (siehe Skizze) und danach eventuell auch solche in den Kanten der $C1/C2$-Matrix durchgeführt werden, wobei jedesmal für das bisher angefallene Datenmaterial der doppelte bivalente Ausgleich umfassendere Informationen liefert.

Polyvalenter Ausgleich

Die Funktion (V) der Tab. I beschreibt einen PENTAVALENTEN Ausgleich, d.h. einen Ausgleich für 5 Reihen paralleler Merkmalsgrößen $\{y_i, x(1)_i, x(2)_i, x(3)_i, x(4)_i\}$. Eine anschauliche Deutung eines derartigen Ausgleiches ist kaum möglich, doch läßt sich sagen, daß die Merkmalsgrößen $x(J)_i$ hier IMPLIZIT verschachtelt sind. Bei Ausgleichsfunktionen des Typs(2) endet die EXPLIZITE Darstellungsmöglichkeit (= selbständige Teilfunktionen $Z1$ und $Z2$) bei trivalenten Ansätzen. Für den polyvalenten Ausgleich müssen speziell in der analytischen Chemie noch Hypothesen und Arbeitstechniken der zeitsynchronen Mehrfachmessung von Merkmalen entwickelt werden. Als Beispiel eines impliziten trivalenten Ausgleiches können die obigen Potentialmessungen dienen, wenn T nicht konstant gehalten, sondern gleichzeitig bei den Messungen variiert bzw. zusätzlich gemessen wird. Zwar bleibt in diesem Fall die Formel (7) erhalten, doch ist

$$Y = \ln C_i;\ Z1 = \frac{1}{T_i};\ Z2 = \frac{\mathcal{E}_i}{T_i}$$

zu setzen.

Abschließend sei darauf hingewiesen, daß die Auswahlmöglichkeiten bei einer universellen Ausgleichsfunktion mit 3 Konstanten vom Typ

$$Y = [A] \cdot Z1 + [B] \cdot Z2 + [C] \cdot Z3$$

noch wesentlich erweitert werden können. Für diese Grundfunktion existieren 3 reduzierte Funktionen mit 2 Konstanten und ebenfalls 3 Funktionen mit nur 1 Konstante. Über mathematische Struktur und Formulierung einer ALGOL-Prozedur AUSGL 3 wird in einer weiteren Arbeit berichtet.

Elektronische Datenverarbeitung

Wie in den Arbeiten I, II, III[1–3] werden nachfolgend Programme in der problemorientierten Sprache ALGOL (ALGO-rithmic L-anguage) unter Verwendung der für das Codesystem ALCOR CCIT zulässigen Zeichen formuliert. In Arbeit I wurde hierzu eine Auswahl an einführender Literatur genannt.

Ebenso wie bereits bei der Korrelationsrechnung[3] ist es auch hier sehr vorteilhaft, das mathematische Modell der Ausgleichsrechnung in einer JENSEN-Prozedur (Beschreibung z.B. in [4]) zu konservieren. Die Prozedur-Vereinbarung beginnt in diesem Fall mit:

'PROCEDURE' AUSGL 2 (N, I, Y, Z1, Z2, T1, T2, T3, T4);...

Als Prozedur-Name wurde AUSGL 2 gewählt, da eine universelle Ausgleichsfunktion mit 2 Konstanten formuliert ist. In der Liste der FORMALEN Parameter stehen ausschließlich die EINGANGS-Informationen.

$n \triangleq \mathrm{N}$ = Datenumfang der parallelen Merkmalsreihen

$i \triangleq \mathrm{I}$ = formale Laufzahl

$Y, Z1, Z2$ = formale Symbole für arithmetische Ausdrücke, gebildet mit den Merkmalsgrößen.

$t_1, t_2, t_3, t_4 \triangleq \mathrm{T1, T2, T3, T4}$ = Statistische Größen der t-Verteilung.

Die t-Größen sind in Tab. II noch näher definiert und in der Literatur vielfach in Tabellenform zusammengestellt (siehe z.B.[5–8]).

Die AUSGANGS-Informationen [A], [B], [s_K], [s_A], [s_B] und eventuelle Größen i, v_i, τ_i des Ausreißer-Testes werden nicht gespeichert, sondern direkt ausgedruckt. Die Prozedur AUSGL2 besitzt analog den Korrelationsprozeduren KORR und TEST[3] den Charakter eines SCHWARZEN KASTENS (black box) und kann daher allein über AKTUELLE INPUT/OUTPUT-Größen in „Betrieb" genommen werden, wie dies Abb. 1 verdeutlichen soll.

Damit eröffnet sich die Möglichkeit, selbst komplizierte Ausgleichsrechnungen mit einem Minimum an mathematischen Kenntnissen im Rahmen chemischer oder beliebig anderer Problemstellungen sowohl planen als auch durchführen zu können. Die erforderliche Programmierarbeit beschränkt sich dabei auf die Erstellung eines zumeist sehr einfachen Rahmenprogrammes, das geeignete AUFRUFE der Prozedur enthält. Liegen für die Beispiele der Tab. I für alle Merkmalsgrößen z.B. jeweils $n = 40$ Einzeldaten vor, so genügen als Anweisung zur Durchrechnung allein die folgenden Aufrufe im Rahmenprogramm:

```
(I)   AUSGL 2 (40, I, Y[I], 1, LN(X[I])/LN(10), T1, T2, T3, T4);
(II)  AUSGL 2 (40, I, Y[I], X[I], X[I]XX[I], T1, T2, T3, T4);
(III) AUSGL 2 (40, I, LN(C[I]), 1, X[I], T1, T2, T3, T4);
(IV)  AUSGL 2 (40, I, Y[I], X1[I], X2[I], T1, T2, T3, T4);
(V)   AUSGL 2 (40, I, Y[I], X1[I] − X2[I], X3[I]/X4[I], T1, T2, T3, T4);
```

Eine ausführlichere Beschreibung des BLACK-BOX-Prinzipes brachte bereits Arbeit III.[3]

MATHEMATISCHE STRUKTUR

Grundsummen und Determinanten

Grundlage der nachfolgend beschriebenen Rechengänge bilden die Elementarbeziehungen (2) und (3) bzw. (4) und (5). Die mathematische Aufschlüsselung, insbesondere der Minimumsbedingungen, durch partielle Differentiation wird in

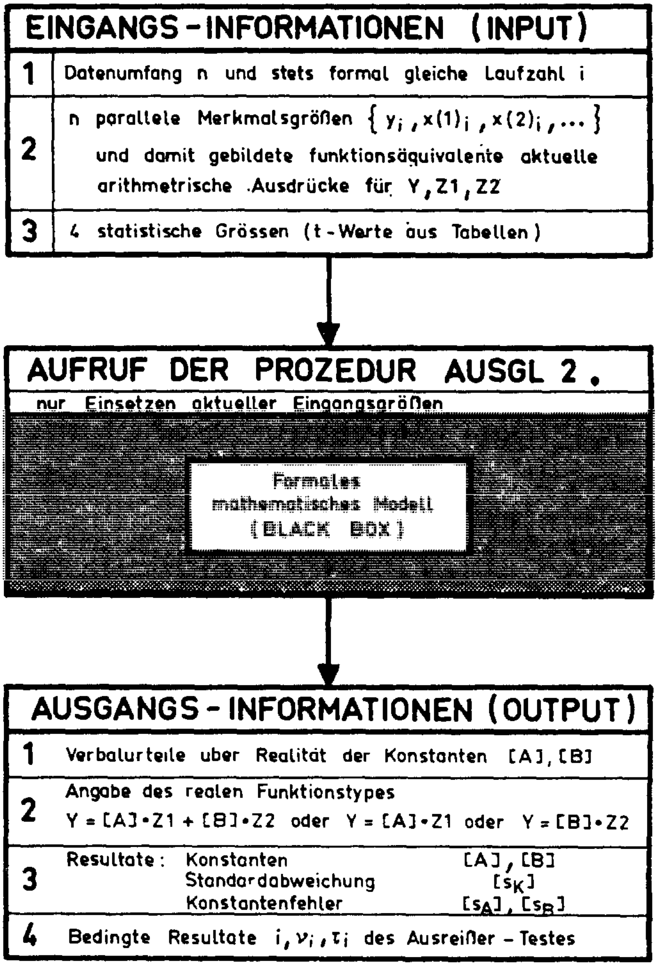


ABB. 1.—INPUT/OUTPUT-System der Prozedur AUSGL 2.

dieser Arbeit übergangen, da sie in der Literatur mehrfach ausführlich beschrieben ist (siehe z.B.[8]).

Der eigentliche Rechengang beginnt mit der Bildung von 5 Grundsummen S1 bis S5, die man zu 3 Determinanten **D**, D_A, D_B zusammenfassen kann, wie dies Tab. II unter [1] und [2] zeigt. Wird z.B. die Funktion (I) aufgerufen, so werden aktuell die Rechenoperationen

$$\mathrm{S1} = \sum_1^n 1\cdot 1 = n; \quad \mathrm{S2} = \sum_1^n \log x_i; \quad \mathrm{S3} = \sum_1^n (\log x_i)^2; \quad \mathrm{S4} = \sum_1^n y_i; \quad \mathrm{S5} = \sum_1^n y_i \,.\, \log x_i$$

durchgeführt. In der Prozedur AUSGL2 wird nur die Hauptdeterminante **D** gesondert berechnet, während für die nur einmalig rechnerisch verwertbaren Determinanten D_A, D_B direkt die S-Ausdrücke formuliert sind. Aufrufe der Prozedur mit

$$Z1 = 0 \quad \text{oder} \quad Z2 = 0 \quad \text{oder} \quad Z1 = Z2$$

führen stets zu **D** = 0 und sind sinnlos. Zur Vermeidung schädlicher Auswirkungen

Tabelle II.—Mathematische Struktur der Ausgleichsrechnung mit 2 Konstanten (fett gedruckte Symbole = ALGOL – Namen)

<table>
<tr><th colspan="2">1 | Grundsummen</th><th colspan="2">2 | Determinanten</th></tr>
<tr><td>$\mathbf{S1} = \sum_1^n \mathbf{Z1} \cdot \mathbf{Z1}$
$\mathbf{S2} = \sum_1^n \mathbf{Z1} \cdot \mathbf{Z2}$
$\mathbf{S3} = \sum_1^n \mathbf{Z2} \cdot \mathbf{Z2}$</td><td>$\mathbf{S4} = \sum_1^n \mathbf{Z1} \cdot \mathbf{Z1}$
$\mathbf{S5} = \sum_1^n \mathbf{Z2} \cdot \mathbf{Y}$
mit $n = \mathbf{N}$</td><td colspan="2">$\mathbf{D} = \mathbf{S1} \cdot \mathbf{S3} - \mathbf{S2} \cdot \mathbf{S2}$
$\mathbf{D_A} = \mathbf{S3} \cdot \mathbf{S4} - \mathbf{S2} \cdot \mathbf{S5}$
$\mathbf{D_B} = \mathbf{S1} \cdot \mathbf{S5} - \mathbf{S2} \cdot \mathbf{S4}$</td></tr>
<tr><th colspan="4">3 | Primärresultate</th></tr>
<tr><td colspan="4">$\mathbf{A} = [A] = D_A/D = (\mathbf{S3} \times \mathbf{S4} - \mathbf{S2} \times \mathbf{S5})/\mathbf{D}$
$\mathbf{B} = [B] = D_B/D = (\mathbf{S1} \times \mathbf{S5} - \mathbf{S2} \times \mathbf{S4})/\mathbf{D}$
$\mathbf{SK} = [s_K] = \sqrt{\frac{1}{n-2} \sum_1^n \nu_i^2}$ mit $\mathbf{NY[I]} = \nu_i = \mathbf{A} \times \mathbf{Z1} + \mathbf{B} \times \mathbf{Z2} - \mathbf{Y}$
$\mathbf{SA} = [s_A] = \sqrt{\mathbf{SK}^2 \times \mathbf{S3}/\mathbf{D}}$ und $\mathbf{SB} = [s_B] = \sqrt{\mathbf{SK}^2 \times \mathbf{S1}/\mathbf{D}}$</td></tr>
<tr><th colspan="4">4 | Boole'sche Variable und Primär-Entscheidungen</th></tr>
<tr><td colspan="4">Prüfgrößen TAU: $\tau_A = |\mathbf{A}|/\mathbf{SA}$ und $\tau_B = |\mathbf{B}|/\mathbf{SB}$
V1 WAHR für $\tau_A \geqq t_1$; NICHT WAHR für $\tau_A < t_1$
V2 WAHR für $\tau_B \geqq t_1$; NICHT WAHR für $\tau_B < t_1$</td></tr>
<tr><td colspan="4">Wenn (V1 UND V2) WAHR dann (V1) NICHT WAHR setzen und weiter bei [7] sonst nach Ausgabe der Wahrheitswerte von V1 und V2 weiter bei [5]</td></tr>
<tr><th colspan="2">5 | Rechengang für $Y = [A] \cdot Z1$</th><th colspan="2">6 | Rechengang für $Y = [B] \cdot Z2$</th></tr>
<tr><td colspan="2">$\mathbf{A} = \mathbf{S4}/\mathbf{S1}$ und $\mathbf{B} = \mathbf{SB} = \phi$ gesetzt
$\mathbf{SK} = \sqrt{\frac{1}{n-1} \sum_1^n \nu_i^2}$ mit $\mathbf{NY[I]} = \mathbf{A} \times \mathbf{Z1} - \mathbf{Y}$
$\mathbf{SA} = \sqrt{\mathbf{SK}^2/\mathbf{S1}}$; neues V1 mit t_2</td><td colspan="2">$\mathbf{B} = \mathbf{S5}/\mathbf{S3}$ und $\mathbf{A} = \mathbf{SA} = \phi$ gesetzt
$\mathbf{SK} = \sqrt{\frac{1}{n-1} \sum_1^n \nu_i^2}$ mit $\mathbf{NY[I]} = \mathbf{B} \times \mathbf{Z2} - \mathbf{Y}$
$\mathbf{SB} = \sqrt{\mathbf{SK}^2/\mathbf{S3}}$; neues V2 mit t_2</td></tr>
<tr><td colspan="2">Wenn (neues V1) WAHR, dann zu [7] sonst Verbalurteil A = O und zu [6]</td><td colspan="2">Wann (neues V2) WAHR, dann (V1) NICHT WAHR setzen und zu [7] sonst Verbalurteil B = O und ENDE</td></tr>
<tr><th colspan="4">7 | Resultatausgabe und Ausreißer-Test</th></tr>
<tr><td colspan="4">AUSGABEANWEISUNG für [A], [B], $[s_K]$, $[s_A]$, $[s_B]$
AUSGABE von i, ν_i, τ_i, wenn $\tau_i = |\mathbf{NY[I]}|/\mathbf{SK} \geqq t_3$ [3] bzw. $\tau_i \geqq t_4$ [5] oder [6]
Wenn (VI) WAHR, dann zurück nach [6], sonst ENDE</td></tr>
<tr><td colspan="4">Integralgrenzen t der t-Verteilung für Vergleiche</td></tr>
<tr><td colspan="2">S = 99% T1 = t_1 für $f = n - 2$
T2 = t_2 für $f = n - 1$</td><td colspan="2">S = 95% T3 = t_3 für $f = n - 2$
T4 = t_4 für $f = n - 1$</td></tr>
</table>

enthält die Prozedur AUSGL2 für entsprechende Aufruf-Fehler einen „Notausgang", wie später noch ausführlicher gezeigt wird.

Primärresultate und Primärentscheidung

Aus Grundsummen und Determinanten folgen die 5 Primärresultate [A], [B], $[s_K]$, $[s_K]$, $[s_B]$ nach den Formeln [3] der Tab. III. Die zur Bildung von $[s_K]$ erforderliche Quadratsumme der Einzelabweichungen kann formal auch nach

$$\sum_1^n v_i^2 = \sum_1^n Y^2 - [A] \cdot S4 - [B] \cdot S5$$

berechnet werden. Die rechnerische Genauigkeit der Differenzbildung von Summen hängt jedoch stark von der Größe der Summen ab. Bei kleinen Differenzen auf großen Summengliedern besteht die Gefahr, daß die zwangsläufige Begrenzung der Zahlendarstellung in elektronischen Rechenanlagen zum Tragen kommt, wodurch sehr ungenaue oder sogar falsche Resultate erhalten werden können. Dagegen lassen sich die Einzelabweichungen

$$v_i = [A] \cdot Z1 - [B] \cdot Z2 - Y$$

sehr genau berechnen, da die resultierenden Differenzen noch relativ groß sind. Die gleiche Größenordnung der v_i-Werte führt auch zu einem numerisch stets zuverlässigen Summenwert der Quadrate v_i^2. Ein weiterer Grund für einen Rechengang mit Einzelabweichungen ist im vorliegenden Fall die ohnehin erforderliche Kenntnis der v_i-Werte zur Durchführung des abschließenden Ausreißer-Testes.

Nach Berechnung der Primärresultate muß geprüft werden, ob die ermittelten Konstanten [A] und [B] sich im Rahmen ihrer Fehlergrößen $[s_A]$ bzw. $[s_B]$ tatsächlich real von Null unterscheiden. Hierzu vergleicht man die Absolutwerte τ (TAU) der Relationen

$$\tau_A = \frac{|[A]|}{[s_A]} \quad \text{und} \quad \tau_B = \frac{|[B]|}{[s_B]} \tag{9}$$

mit den Integralgrenzen t_1 der t-Verteilung für
den Freiheitsgrad $f = n - 2$ (2 Konstanten.) und
der Statistischen Sicherheit $S = 99\%$ (level of significance 0,01).

Es ist zweckmäßig, diese arithmetischen Vergleichsausdrücke als Boole'sche Variable $V1$ und $V2$ zu verschlüsseln, wie dies in [4] der Tab. II formuliert ist.

V. WAHR ist der Aussage äquivalent, daß die betreffende Konstante SIGNIFIKANT VON NULL VERSCHIEDEN und damit real ist.

V. NICHT WAHR entspricht der Aussage, daß für die betreffende Konstante ein UNTERSCHIED ZU NULL NICHT FESTSTELLBAR (allenfalls nur wahrscheinlich) und sie damit nicht real ist.

Die Primärentscheidung folgt aus einer KONJUNKTIVEN logischen Verknüpfung der Boole'schen Variablen $V1$ und $V2$. Nur für „$V1$ UND $V2$ WAHR", d.h. für Realität beider Konstanten [A] und [B] stellen die Primärresultate bereits das Endergebnis dar und die Rechnung ist nach dem AusreißerTest zu beenden. Wenn dagegen „$V1$ UND $V2$ NICHT WAHR" gefunden wird, was stets für „[A] ODER [B] ODER BEIDE nicht real" zutrifft, so sind Folge-Rechengänge für die reduzierten Funktionen (4) erforderlich. Die Primärresultate besitzen in diesem Fall keinen Aussagewert und könne vom menschlichen oder maschinellen Rechner „vergessen" werden, wodurch die Symbole der Größen für die neuen Rechengänge zur Verfügung stehen.

Folge-Rechengänge und Sekundär-Entscheidungen

Folge-Rechengänge auf Grund einer entsprechenden Primärentscheidung werden stets für die beiden reduzierten Funktionen (4) durchgeführt. Die Formeln des 1. Folge-Rechenganges für $Y = [A] \cdot Z1$ sind in [5] der Tab. II zusammengestellt. Man setzt $[B] = [s_B] = 0$ und errechnet unter Verwendung der Grundsummen S1 und S4 neue Resultate für [A], $[s_K]$ und $[s_A]$, wobei auch hier die Quadratsumme zum $[s_K]$-Wert über die Einzelabweichungen $v_i = [A] \cdot Z1 - Y$ gebildet wird. Analog (9) ergibt sich ein neuer τ_A-Wert, der mit einem t_2 zu vergleichen ist, das für $f = n - 1$ (1 Konstante!) und $S = 99\%$ einer Tabelle entnommen wird. Der Vergleich führt zu einer neuen Boole'schen Variablen $V1$, die die 1. Sekundärentscheidung bestimmt.

Ist das neu errechnete [A] real von Null verschieden („neues $V1$ wahr"), so stellen die Resultate des 1. Folge-Rechenganges sowie eventuelle Resultate des Ausreifer-Testes ein Teilergebnis der Auswertung dar. Ein „neues $V1$ nicht wahr" zeigt dagegen eindeutig, daß für die vorliegenden Datenreihen in Verbindung mit dem Funktionsteil $Z1$ kein reales [A] nachweisbar ist.

Die Formeln des 2. Folge-Rechenganges für $Y = [B] \cdot Z2$ sind in [6] der Tab. II zusammengestellt. Es werden zunächst $[A] = [s_A] = 0$ gesetzt und danach unter Verwendung der Grundsummen S3 und S5 neue Resultate für [B], $[s_K]$ und $[s_B]$ errechnet. Die Quadratsumme zum $[s_K]$-Wert wird wie bisher über die Einzelabweichungen, hier $v_i = [B] \cdot Z2 - Y$, gebildet. Analog (9) ergibt sich ein neuer τ_B-Wert, der wie das neue τ_A nach dem 1. Folge-Rechengang mit t_2 verglichen wird. Der Vergleich führt zu der neuen Boole'schen Variablen $V2$, die die 2. Sekundärentscheidung bestimmt.

Ist das neu errechnete [B] real von Null verschieden („neues $V2$ wahr"), so bilden die Resultate des 2. Folge-Rechenganges sowie eventuelle Resultate des Ausreißer-Testes das abschließende Teilergebnis der Auswertung. Ein „neues $V2$ nicht wahr" zeigt dagegen eindeutig, daß für die vorliegenden Datenreihen in Verbindung mit dem Funktionsteil $Z2$ kein reales [B] nachweisbar ist.

Der Fall, daß die reduzierten Funktionen JEDE FÜR SICH reale Konstanten [A] bzw. [B] und somit vollständige Auswertungsergebnisse liefern, ist keinesfalls ungewöhnlich. Die beste funktionelle Interpretation des verarbeiteten Datenmaterials gibt dann diejenige Funktion mit der kleineren Standardabweichung $[s_K]$.

Ausreisser-Test

Nach Durchführung der Ausgleichs-Rechengänge ist es zur Sicherstellung der Zuverlässigkeit der Resultate notwendig, die jeweiligen n Einzelabweichungen v_i auf ungewöhnlich große Werte zu prüfen. Ein durch

$$|v_i| = [s_K] \cdot t \tag{10}$$

definierter absoluter Fehlerbereich darf nach der mathematischen Theorie statistischer Verteilungen nicht beliebig oft und weit überschritten werden, wenn bei der Datenermittlung tatsächlich nur zufallsbedingte Einflüsse wirksam waren. Zulässige Größen und Zahl der Überschreitungen der Fehlerbereiche sind über die Verteilungsgröße t

vom Freiheitsgrad f und der statistischen Sicherheit S abhängig. Die Zulässigkeitsbedingung wird zweckmäßig über Vergleiche von aus (10) folgenden n Prüfgrößen

$$\tau_i = \frac{|\nu_i|}{[s_K]} \tag{11}$$

mit $t = t(S)$-Werten der t-Verteilung formuliert. „Überzufällige" Sondereinflüsse sind nicht nachweisbar, wenn

$$\tau_i < t(95)$$

$$\text{und} \quad t(95) \leqq \tau_i < t(99) \text{ für je } 1\nu_i \text{ unter 20 Daten}$$

$$\text{und} \quad t(99) \leqq \tau_i < t(99{,}9) \text{ für je } 1\nu_i \text{ unter 100 Daten}$$

$$\text{und} \quad \tau_i \geqq t(99{,}9) \text{ für je } 1\nu_i \text{ unter 1000 Daten}$$

gefunden wird. ν_i-Werte und zugehörige Merkmalsgrößen, die die Zulässigkeitsbedingung nicht erfüllen, werden als AUSREISSER bezeichnet. Ausreisser bewirken eine Verzerrung der Resultate der Ausgleichsrechnung. Daher muß die gesamte Rechnung in solchen Fällen unter Fortlassen der Ausreißer-Größer bzw. Ersatz durch Daten eines neuen Versuches wiederholt werden.

Im Rahmen der ALGOL-Prozedur AUSGL2 beschränkt sich der Ausreißer-Test auf das Auffinden und Ausdrucken der Datennummer i, der Abweichung ν_i und der Prüfgröße τ_i für alle Abweichungen mit

$$\frac{|\nu_i|}{[s_K]} = \tau_i \geqq t(95) \tag{12}$$

wobei $t(95) = t_3$ mit $f = n - 2$ für die Hauptfunktion (2) und $t(95) = t_4$ mit $f = n - 1$ für die reduzierten Funktionen (4) gesetzt wird. Ob die ausgedruckten Größen tatsächlich Ausreißer sind, muß nach Anzahl und Vergleich von τ_i mit entsprechenden Größen $t(99)$ und $t(99{,}9)$ extern entschieden werden. Es sei hier darauf hingewiesen, daß ein analoger Ausreißer-Test bereits in der Arbeit I (Modellanalysen) formuliert und durchgeführt wurde.

PROGRAMMIERUNG

Flussdiagramm

Abb. 2 zeigt das vollständige Ablaufschema der Prozedur AUSGL2. Aus dem Flußdiagramm kann man unmittelbar die möglichen Rechenabläufe entnehmen.

(1) Ist [A] UND [B] real von Null verschieden, so wird auf Grund der äquivalenten Primär-Entscheidung „*V*1 UND *V*2 wahr" der 'THEN'-Zweig eingeschlagen und zunächst formal „*V*1 nicht wahr" gesetzt. Danach werden über die Marke AUSGABE die Primärresultate und eventuell Werte zum Ausreißer-Test ausgedruckt. Wegen „*V*1 nicht wahr" führt die Ausgangsentscheidung folgerichtig zum ENDE der Rechnung.

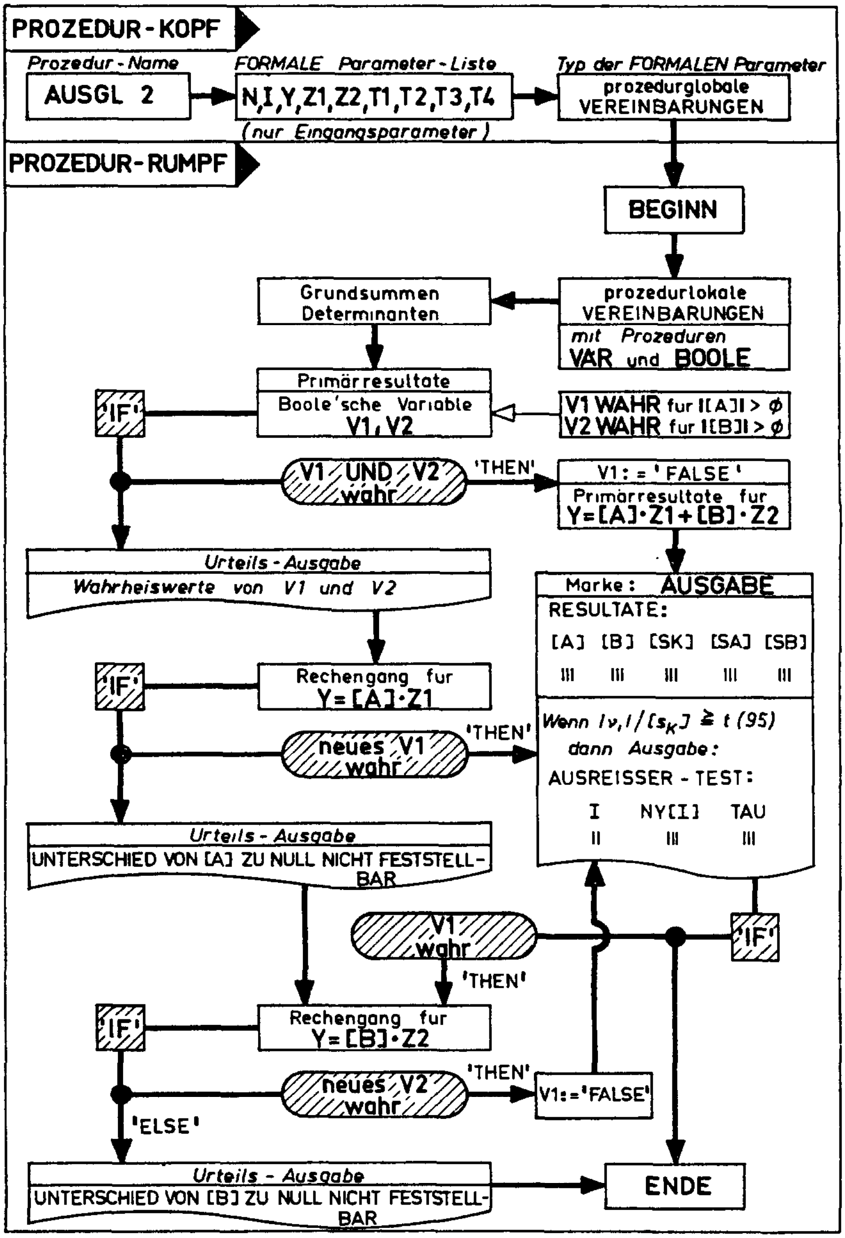


Abb. 2.—Flußdiagramm der ALGOL-Prozedur AUSGL 2.

(2) Ist [A] UND bzw. ODER [B] nicht real von Null verschieden, so wird der Weg (1) „verschlossen". Nach Ausdrucken der möglichen Ursache

$V1$ WAHR UND $V2$ NICHT WAHR
oder $V1$ NICHT WAHR UND $V2$ WAHR
oder $V1$ NICHT WAHR UND $V2$ NICHT WAHR

wird der Rechengang für die reduzierte Funktion $Y = [A] \cdot Z1$ durchgeführt, wobei $[B] = [s_B] = 0$ gesetzt und auch ein neuer Wahrheitswert für $V1$ erhalten wird.

(3) Sofern das neu errechnete [A] real von Null verschieden ist („neues $V1$ wahr"), führt ein 'THEN'-Zweig direkt zur Marke AUSGABE, wo die neuen Resultate und eventuell Werte des Ausreißer-Testes ausgedruckt werden. Wegen „$V1$ wahr" schließt sich sodann noch der Rechengang für die reduzierte Funktion $Y = [B] \cdot Z2$ an. Dieser Rechengang wird auch direkt aktiviert, wenn das neu errechnete [A] nicht real von Null verschieden ist („neues $V1$ nicht wahr"), wobei vorher noch das Urteil

UNTERSCHIED VON [A] ZU NULL NICHT FESTSTELLBAR

ausgedruckt wird.

(4) Im Rechengang für $Y = [B] \cdot Z2$ wird $[A] = [s_A] = 0$ gesetzt und auch ein neuer Wahrheitswert für $V2$ ermittelt. Ist das neu errechnete [B] real von Null verschieden („neues $V2$ wahr"), so wird in einem 'THEN'-Zweig formal „$V1$ nicht wahr" gesetzt. Danach werden über die Marke AUSGABE die neuen Resultate und eventuell Werte des Ausreißer-Testes ausgedruckt. Wegen „$V1$ nicht wahr" führt die Ausgangs-Entscheidung wie bei (1) zum ENDE der Rechnung. Für „neues $V2$ nicht wahr" führt ein 'ELSE'-Zweig zum Ausdrucken des Urteils

UNTERSCHIED VON [B] ZU NULL NICHT FESTSTELLBAR

und danach zum ENDE der Rechnung.

ALGOL-Prozeduren und Rahmenprogramm

Abbildung 3 bringt die ALGOL-Formulierung der Prozedur AUSGL2. Sie enthält im Prozedur-Rumpf die weitere JENSEN-Prozedur VAR zur Berechnung der Summe von Abweichungsquadraten, die insgesamt 3 mal mit aktuellen Größen aufgerufen wird, sowie eine einfache Prozedur BOOLE zur Berechnung von Wahrheitswerten, die 4 mal aufgerufen wird. Im Rahmen der Rechenanweisungen ist unmittelbar nach der Berechnung der Hauptdeterminanten **D** eine Bedingte Anweisung

```
'IF' D 'EQUAL' 0 'THEN' 'BEGIN'
  WRITE ("< ≡ AUFRUF-FEHLER:  Z = 0   ODER   Z1 = Z2,
   DAHER   D = 0"); 'GO TO' ENDE 'END';
```

formuliert, die die Auswirkung eines fehlerhaften Prozedur-Ausfrufes im Rahmenprogramm durch Auslassen aller weiteren Rechenanweisungen im Prozedur-Rumpf eliminiert. Ohne diesen „Notausgang" würde die rechnerische Auswertung eines im Rahmenprogramm formulierten Problems mit maschineller Fehlermeldung „DIVISION DURCH NULL" automatisch gestoppt werden, was insbesondere bei längeren Programmen zu einer beträchtlichen Erhöhung des Zeitbedarfes führt.

Die Prozedur AUSGL2 ist erprobt und braucht von einem Benützer nur sorgfältig abgeschrieben und an ein Rechenzentrum gegeben zu werden. Die zukünftige Arbeit beschränkt sich sodann auf das Schreiben problemspezifischer Rahmenprogramme, in die die Prozedur lediglich im Vereinbarungsteil durch den Hinweis

```
'PROCEDURE' AUSGL 2 (N,I,Y,Z1,Z2,T1,T2,T3,T4);
  'REAL' Y, Z1, Z2,T1, T2,T3,T4 ; 'INTEGER' N,I ;

  'BEGIN'  'REAL' S1,S2,S3,S4,S5,P1,P2,P3,D,A,B,SK,SA,SB, TAU ;
           'BOOLEAN' V1,V2 ;     'ARRAY' NY [1:N] ;

   'PROCEDURE' VAR (N,I,A,B,Y,Z1,Z2,NY,SK);
     'REAL' A,B,Y,Z1,Z2,SK ;  'INTEGER' N,I ;    'ARRAY' NY ;
     'BEGIN' SK: = 0; 'FOR' I := 1 'STEP' 1 'UNTIL' N 'DO'
       'BEGIN' NY[I]: = A × Z1 + B × Z2 - Y ; SK := SK+NY[I]×NY[I] 'END''END';

   'PROCEDURE' BOOLE (U,SU,T,V);
     'REAL' U,SU,T; 'BOOLEAN' V ;  V:= ABS (U/SU) 'NOTLESS' T ;

   S1:= S2:= S3:= S4:= S5:= 0 ;
   'FOR' I:= 1 'STEP' 1 'UNTIL' N 'DO' 'BEGIN'  P1:= Z1; P2:= Z2; P3:=Y;
     S1:= S1 + P1 × P1 ;  S2:= S2 + P1 × P2;  S3:= S3 + P2 × P2 ;
     S4:= S4 + P1 × P3 ;  S5:= S5 + P2 × P3   'END';

   D:= S1 × S3 - S2 × S2 ;   'IF' D 'EQUAL' 0  'THEN''BEGIN'
    WRITE ("<≡ AUFRUF-FEHLER: Z=0␣ODER␣Z1=Z2, DAHER␣D = 0") ;
                                      'GO TO' ENDE 'END';

   A:= (S3×S4 - S2×S5)/D ;    B:= (S1×S5 - S2×S4)/D ;
   VAR (N,I,A,B,Y,Z1,Z2,NY,SK);  SK := SK/(N-2);
   SA:= SQRT (SK×S3/D); SB:= SQRT (SK×S1/D); SK:= SQRT (SK);
   BOOLE (A,SA,T1,V1);  BOOLE (B,SB,T1,V2);

   'IF' V1 'AND' V2 'THEN' 'BEGIN'
     WRITE ("<≡≡ FUNKTION:␣Y=[A]× Z1+[B]×Z2") ;
     V1: = 'FALSE' ; 'GO TO' AUSGABE   'END';

     'IF' V1 'THEN' WRITE ("<≡≡ V1␣WAHR")
             'ELSE' WRITE ("<≡≡ V1␣NICHT␣WAHR") ;
     'IF' V2 'THEN' WRITE ("5␣UND5␣V2␣WAHR")
             'ELSE' WRITE ("5␣UND5␣V2␣NICHT␣WAHR");

   T3:= T4 ;
   A:= S4/S1; B:= SB:= 0.0 ; VAR (N,I,A,0,Y,Z1,0,NY,SK);
   SK:= SK/(N-1);  SA:= SQRT (SK/S1); SK:= SQRT (SK);
   BOOLE (A,SA,T2,V1); 'IF' V1 'THEN' 'BEGIN'
    WRITE ("<≡≡ RESTFUNKTION:␣Y=[A]×Z1"); 'GO TO' AUSGABE 'END';

    WRITE ("<≡≡ UNTERSCHIED␣VON␣[A]␣ZU␣NULL␣NICHT␣FESTSTELLBAR");

M: B:= S5/S3; A:= SA:= 0.0 ; VAR (N,I,0,B,Y,0,Z2,NY,SK);
   SK := SK/(N-1); SB:= SQRT (SK/S3); SK:= SQRT (SK);
   BOOLE (B,SB,T2,V2); 'IF' V2 'THEN'
     WRITE ("<≡≡ RESTFUNKTION :␣Y = [B] × Z2")
                                     'ELSE' 'BEGIN'
     WRITE ("<≡≡ UNTERSCHIED␣VON␣[B]␣ZU␣NULL␣NICHT␣FESTSTELLBAR");
                   'GO TO' ENDE  'END' ;

   V1:= 'FALSE';

AUSGABE: WRITE ("<≡≡ RESULTATE:<≡5␣[A]14␣[B]14␣[SK]13␣[SA]13␣[SB]");
   PRINT (A,B,SK,SA,SB);
   'FOR' I := 1 'STEP' 1 'UNTIL' N 'DO' 'BEGIN'
     TAU:= ABS (NY[I])/SK ;
     'IF' TAU 'NOTLESS' T3 'THEN' 'BEGIN'
       WRITE ("<≡≡ AUSREISSER-TEST:<≡14␣ I 6␣NY[I]13␣TAU");
       PRINT (I,NY[I],TAU) 'END' 'END';
  'IF' V1 'THEN' 'GO TO' M ;

ENDE: 'END' PROZEDUR  AUSGL 2 ;
```

Abb. 3.—ALGOL-Formulierung der Prozedur AUSGL 2.

... HIER AUSGL2 EINLESEN ...

eingefügt und im Anweisungsteil durch Aufrufe mit aktuellen Parametern rechnerisch aktiviert wird. Der „Schwarze Kasten" der Prozedur AUSGL2 besteht hier wie bei jeder Prozedur aus einer separaten LochstreifenRolle (in Sonderfällen ein Lochkartenstapel), der bei Bedarf auch schnell vervielfältigt und an andere Interessenten weitergegeben werden kann. Bei Schreiben des Datenstreifens mit aktuellen Daten muß darauf geachtet werden, daß die Reihenfolge der Daten mit der Reihenfolge in den Leseanweisungen des Rahmenprogrammes übereinstimmt. Im folgenden wird die Erstellung eines speziellen Rahmenprogrammes unter Verwendung der Prozedur AUSGL2 an einem Beispiel gezeigt.

BEISPIEL

Problemstellung

Bei flammenphotometrischen Analysenverfahren findet man in Bereichen kleiner Konzentrationen C im allgemeinen einen linearen Zusammenhang zwischen C und meßbarer Strahlungsintensität I der Flamme. In Bereichen höherer Konzentration resultieren jedoch bei Messungen der Resonanz-Strahlung mehr oder minder stark gekrümmte Eichkurven $C = F(I)$, da Effekte der SELBSTABSORPTION und der SELBSTUMKEHR zum Tragen kommen. Ausführlicher wird hierüber z.B. in [9] berichtet. Bei reiner Selbstabsorption sollen die Eichkurven durch Funktionen der Form

$$I \sim \sqrt{C} \text{ bzw. } C \sim I^2$$

und bei zusätzlicher Selbstumkehr durch solche der Form

$$I \sim \sqrt[b]{C} \text{ bzw. } C \sim I^b \text{ mit } b > 2$$

beschreibbar sein (siehe auch[10]).

Für die Alkalien Natrium und Kalium ergaben Messungen gleichartig abgestufter Konzentrationen C im MAKRO-Arbeitsbereich, der zu
10 bis 1 μMol cm^{-3}
entspricht 1 bis 0,1 mMol Na bzw. K pro 100 ml Lösung
definiert wurde,[8] unter den nachfolgend beschriebenen Versuchsbedingungen relativ stark gekrümmte Eichkurven, die durch eine geeignete Funktion $C = F(I)$ interpretiert werden sollen.

LÖSUNGSSYSTEME: 6 Meßgruppen mit je 4 vorgegebenen Konzentrationen
10,0/8,0/6,0/4,0/2,0/1,0 μMol · cm^{-3}
an NaCl bzw. KCl in 0,1 m HCl

APPARATIVE PARAMETER: Eppendorf-Flammenphotometer
(Fa. Netheler u. Hinz, Hamburg)
Strahlungsempfänger: RCA 1 P 21
Gasmischung: Propan 200 mm WS
Luft 0,5 kg · cm^{-2}
Natrium: Filter 589 mμ
(Saugspannung 2/Oe 1)
Kalium: Filter 768 mμ
(Saugspannung 3/Oe 1)

NORMIERUNG: 0,1 m HCl auf 0 Skalenteile
$C_0 = 10$ μMol · cm^{-3} (0,01 m) NaCl bzw. KCl/0,1 m HCl
auf $I_0 = 1000$ Skalenteile.

Tabelle III gibt eine Zusammenstellung der gemessenen Intensitäten $I1$ für Na und $I2$ für K, während Abb. 4 die entsprechenden Eichpolygone graphisch verdeutlicht.

Mathematische Rahmenstruktur

Auf Grund der Normierung sollten Konzentrationen $0 \leq C \leq 10$ theoretisch aus

$$C = \frac{C_0}{I_0} \cdot I = 0{,}01 \cdot I$$

folgen. Tatsächlich resultieren unter den vorgegebenen Versuchsbedingungen jedoch nichtlineare Zusammenhänge $C = \mathrm{F}(I)$, wie Abb. 4 zeigt. Unter Berücksichtigung der oben genannten C/I-Zusammenhänge wurde eine Ausgleichsrechnung für 4 verschiedene Funktionstypen (2. Kennziffer) sowohl für die Na-Meßreihe (1. Kennziffer = 1) als auch für die K-Meßreihe (1. Kennziffer = 2) durchgeführt.

TABELLE III.—MEẞWERTE $I1$ UND $I2$ IN SKALENTEILEN FÜR VORGEGEBENE KONZENTRATION C AN NATRIUM BZW. KALIUM IM MAKRO-ARBEITSBEREICH

	Konzentration C	Natrium (589 mμ)		Kalium (768 mμ)	
i	$\mu Mol \cdot cm^{-3}$	$I1$	$\overline{I1}$	$I2$	$\overline{I2}$
1	10,0	1001	999,50 (±1,29)	992	991,25 (±1,50)
2		998		990	
3		999		990	
4		1000		993	
5	8,0	899	900,75 (±1,71)	871	872,00 (±1,42)
6		901		872	
7		900		871	
8		903		874	
9	6,0	759	759,00 (±0,82)	719	720,25 (±1,26)
10		760		720	
11		758		720	
12		759		722	
13	4,0	581	583,00 (±1,83)	535	535,75 (±1,50)
14		585		535	
15		584		535	
16		582		538	
17	2,0	358	356,00 (±1,63)	306	302,00 (±4,08)
18		354		305	
19		356		299	
20		356		298	
21	1,0	195	196,25 (±0,96)	153	150,75 (±1,50)
22		197		150	
23		197		150	
24		196		150	

Bemerkungen: In Klammern ( ) stehen die Gruppenstandardabweichungen s_I. Eine „mittlere" Standardabweichung $[s_I]$ der Intensitätsmessung folgt zu:

$$[s_I] = \sqrt{\frac{1}{12}\sum_{1}^{12} s_I^2} = \pm 1{,}81 \text{ Skalenteilen}$$

1. *Funktion* [11] bzw. [21]

$$C = [A] + [B \cdot I^2 \text{ mit } Y = C_i;\ Z1 = 1;\ Z2 = I1_i^2 \text{ bzw. } I2_i^2$$

Diese Funktion entspricht einer Intensitätsformel:

$$I = \sqrt{b \cdot (C - a)} \text{ wobei } a = [A] \text{ und } b = 1/[B]$$

Für $C = 0$ verbleibt bei $a < 0$ ein Leerwert $I_B = b \cdot \sqrt{-a}$

2. *Funktion* [12] bzw. [22]

$$C = [A] \cdot I + [B] \cdot I^2 \text{ mit } Y = C_i;\ Z1 = I1_i \text{ bzw. } I2_i;\ Z2 = I1_i^2 \text{ bzw. } I2_i^2$$

Diese Funktion entspricht einer Intensitätsformel:

$$I = a \cdot \{\sqrt{1 + b \cdot C} - 1\} \text{ wobei } a = \frac{1}{2} \cdot \frac{[A]}{[B]} \text{ und } b = 4\,\frac{[B]}{[A]^2}$$

$C = 0$ liefert $I = 0$.

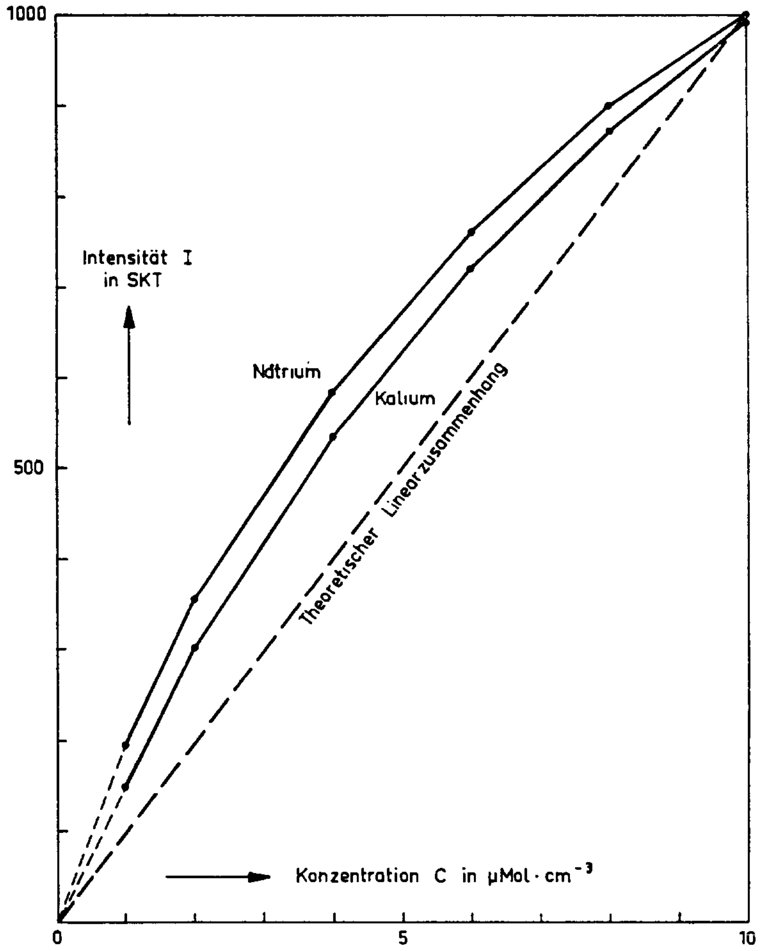


ABB. 4.—Flammenphotometrische C,I-Meßpunkte (I-Mittelwerte) für Natrium und Kalium im Makro-Arbeitsbereich.

3. *Funktion* [13] bzw. [23]

$$\ln C = [A] + [B] \cdot \ln I \text{ mit } Y = \ln C_i;\ Z1 = 1;\ Z2 = \ln I1_i \text{ bzw. } \ln I2_i$$

Diese Funktion entspricht einer Intensitätsformel:

$$I = a \cdot \sqrt[b]{C} \text{ wobei } b = [B] \text{ und } \ln a = -[A]/[B]$$

$C = 0$ liefert $I = 0$. Sofern die Kurvenkrümmung nur durch Selbstabsorption verursacht wird, sollte [B] nicht signifikant von 2 verschieden sein. $[B] > 2$ ist bei zusätzlicher Selbstumkehr zu erwarten. Während die Auswertung von Funktion 1 und 2 mit $[s_c] = [s_K]$ unmittelbar eine im gesamten Arbeitsbereich konstante Standardabweichung in C-Einheiten μMol · cm^{-3} liefert, gilt bei der Funktion 3

$$[s_K] = s(Y) = \frac{[s_c]}{C} = \frac{VK}{100}$$

$$\text{oder } [s_c] = C \cdot [s_K]$$

Im Arbeitsbereich ist hier der Variationskoeffizient VK konstant, wodurch $[s_c]$ im Bereich

$$[s_c]_o = 10 \cdot [s_K] \text{ bis } [s_c]_u = 1 \cdot [s_K]$$

variiert.

4. *Funktion* [14] bzw. [24]

$$\ln \frac{C}{I} = [\mathrm{A}] + [\mathrm{B}] \cdot I \text{ mit } Y = \ln \frac{C_1}{I1_1} \text{ bzw. } \ln \frac{C_1}{I2_1}\,;\; Z1 = 1;\; Z2 = I1_1 \text{ bzw. } I2_1$$

Diese Funktion entspricht einer Konzentrationsformel:

$$C = a \cdot I \cdot e^{b \cdot I} \text{ wobei } \ln a = [\mathrm{A}] \text{ und } b = [\mathrm{B}]$$

$C = 0$ ergibt $I = 0$. Die zu Vergleichen benötigte Standardabweichung $[s_c]$ folgt aus:

$$[s_K]^2 = s(Y)^2 = \left(\frac{[s_c]}{C}\right)^2 + \left(\frac{[s_I]}{I}\right)^2$$

$$\text{bzw. } [s_c] = C \cdot \sqrt{[s_K]^2 - \left(\frac{[s_I]}{I}\right)^2}$$

Im Arbeitsbereich gilt nach Tab. III $[s_I] = \pm 1{,}81$ SKT.

ALGOL-Rahmenprogramm

In Rahmenprogramm werden namentlich nur die aktuellen Größen

T1, T2, T3, T4, I, C[I], I1[I], I2[I]

vereinbart und bis auf I als Eingangs-Informationen eingelesen. $n \mathrel{\hat{=}} \mathrm{N} = 24$ wird direkt numerisch eingesetzt.

Abbildung 5 zeigt das Rahmenprogramm mit der einmaligen Prozedurvereinbarung, den schriftlichen Erläuterungen durch WRITE-Anweisungen und den insgesamt 8 Prozeduraufrufen.

Entsprechend den formulierten Leseanweisungen sind die Eingangsdaten in der Reihenfolge

$$t_1, t_2, t_3, t_4, C_1, I1_1, I2_2, C_2, I1_2, I2_2, \ldots, C_{24}, I1_{24}, I2_{24};$$

im Datenstreifen numerisch aufzulisten. Für die t-Werte findet man in entsprechender Tabelle:

	$S = 99\%$	$S = 95\%$	$S = 99{,}9\%$
$f = n - 2 = 22$	$t_1 = 2{,}819$	$t_3 = 2{,}074$	3,792
$f = n - 1 = 23$	$t_2 = 2{,}807$	$t_4 = 2{,}069$	3,767

Bearbeitungszeiten, Resultate, Urteile

Das vorliegende Beispiel wurde mit einer relativ langsamen Klein-Rechenanlage ZUSE Z23 durchgerechnet, wobei folgende Kenngrößen ermittelt wurden:

Angezeigte Rechenbefehle im Befehlsregister für das Gesamtprogramm: 1834

Einlesen der Prozedur AUSGL 2:	3 min 25 sec
Einlesen des Rahmenprogrammes:	2 min 45 sec
PROGRAMM-EINLESEZEIT PEZ	6 min 10 sec
Daten-Einlesezeit DEZ:	— 20 sec
Rechenzeit RZ, Schnell-Locher-Ausgabe:	10 min —
(Fernschreiber	14 min 20 sec)
ELEKTRONISCHE BEARBEITUNGSZEIT EBZ:	10 min 20 sec
GESAMTZEIT für das Beispiel:	[16 min 30 sec]

```
'BEGIN'
  'REAL' T1,T2,T3,T4 ;
  'INTEGER' I ;
  'ARRAY'C,I1,I2 [1:24] ;

 ( Einlese - STOP  durch  hinreichend  lange  Folge  von  BU - Zeichen )

 < 'PROCEDURE' AUSGL 2  (N,I,Y,Z1,Z2,T1,T2,T3,T4);  ....<

 ( dann  weiter  Rahmenprogramm  einlesen )

  READ (T1,T2,T3,T4);
  'FOR'I := 1'STEP' 1 'UNTIL' 24 'DO' READ (C[I],I1[I], I2[I]);
              5
  WRITE ("< ≡ AUSGLEICHSRECHNUNG␣MIT␣2␣KONSTANTEN
     < ≡ FLAMMENPHOTOMETRIE␣ FUER ␣C = 10␣BIS ␣1␣MIKROMOL/CCM");
             5                         10
  WRITE ("< ≡ ELEMENT␣NATRIUM ␣ ×
             5
          < ≡ [11]␣C[NA] = [A]+[B]×I×I ");
  AUSGL 2 (24,I,C[I],1,I1[I] × I1[I] ,T1,T2,T3,T4);
              5
  WRITE ("< ≡ [12]␣C[Na] = [A]×I+[B]×I×I");
  AUSGL 2  (24,I,C[I],I1[I],I1[I]×I1[I],T1,T2,T3,T4);
              5
  WRITE  ("< ≡ [13]␣LN (C[Na]) = [A]+[B] × LN(I)");
  AUSGL 2  (24,I,LN (C[I]),1, LN (I1[I]), T1,T2,T3,T4);
              5
  WRITE  ("< ≡ [14]␣LN(C[Na]/I) = [A]+[B]×I ");
  AUSGL 2  (24,I,LN(C[I]/I1[I]),1,I1[I], T1,T2,T3,T4);
              5                         11
  WRITE ("< ≡ ELEMENT␣ KALIUM ␣ ×
             5
          < ≡ [21]␣C[K] = [A]+[B]×I × I");
  AUSGL 2 ( 24,I,C[I],1,I2[I]× I2[I],T1,T2,T3,T4 );
              5
  WRITE ("< ≡ [22]␣C[K] = [A]× I+[B]×I×I ");
  AUSGL 2 (  24,I,C[I],I2[I],I2[I]  I2[I],T1,T2,T3,T4);
              5
  WRITE ("< ≡ [23]␣LN (C[K]) = [A]+[B]× LN (I)");
  AUSGL 2  ( 24,I, LN (C[I]),1, LN(I2[I]),T1,T2,T3,T4);
              5
  WRITE ("< ≡ [24]␣LN (C[K]/I) = [A]+[B]×I");
  AUSGL 2 ( 24,I, LN (C[I]/I2[I]),1,I2[I], T1 ,T2 ,T3,T4);

  'END' RAHMENPROGRAMM
```

ABB. 5.—ALGOL-Rahmenprogramm des Beispieles.

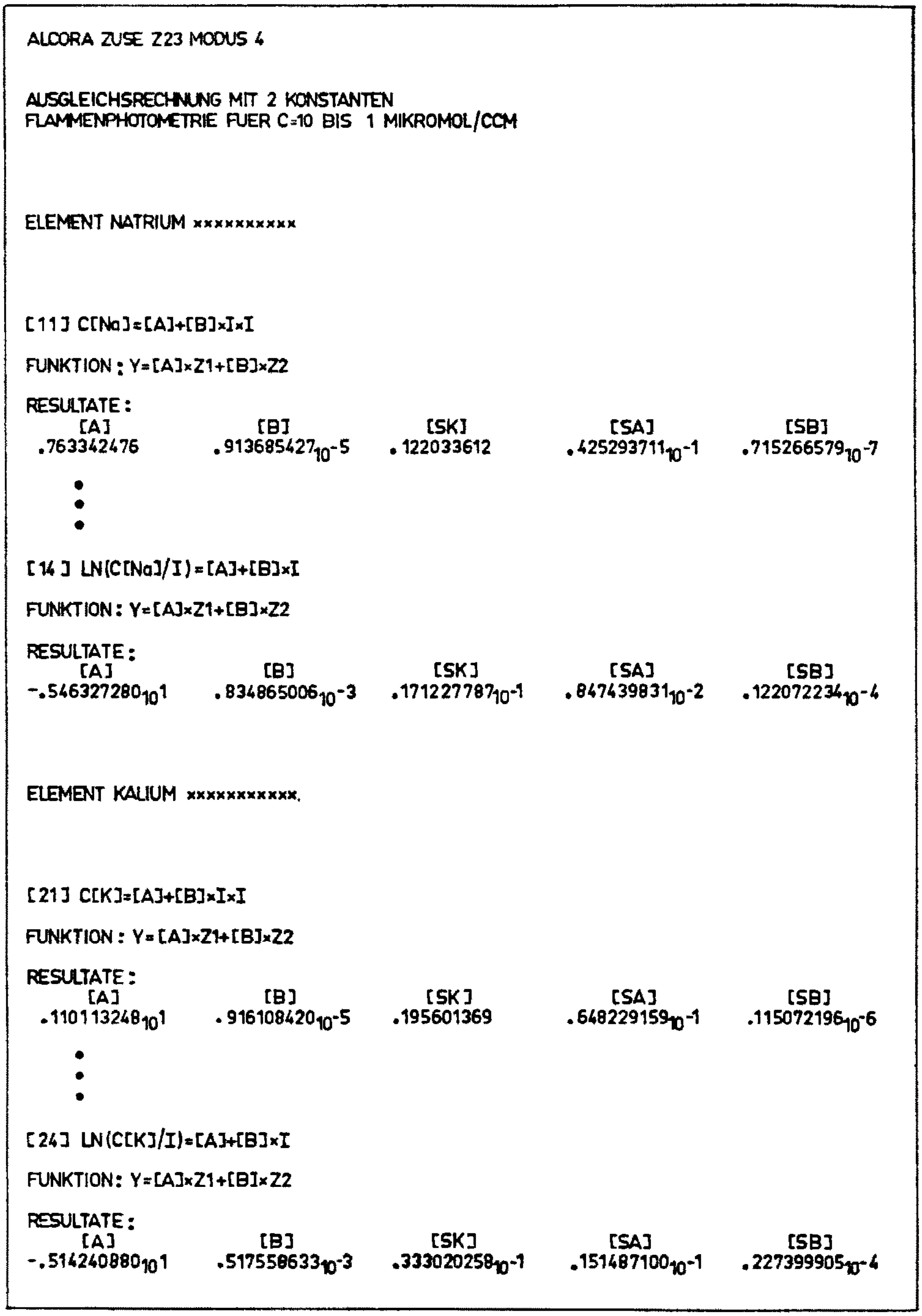
Für die vollständige Durchrechnung und Beurteilung von nur einer der 8 Ausgleichsfunktionen werden nur etwa 1 min 20 sec RZ benötigt. Die Umsetzungszeit des Ergebnis-Lochstreifens des Schnell-Lochers mit einem ALGOL-Schreiber in einen Klarschriftbogen beträgt 4 min.

Tabelle IV gibt eine Zusammenstellung der gerundeten Resultate sowie die aus $[s_{\mathrm{K}}]$ folgenden vergleichbaren Standardabweichungen $[s_{\mathrm{c}}]$ und Variationskoeffizienten *VK* für Konzentrationen *C* der oberen und unteren Grenze des Makro-Arbeitsbereiches. Abbildung 6 zeigt Anfang, Mittelteil und Ende des maschinell erstellten Ergebnis-Bogens.

Diskussion der Ergebnisse

Zunächst ist festzustellen, daß bei allen 4 vorgegebenen Funktionen real von Null verschiedene Konstanten [A] und [B] gefunden wurden. In keinem Fall wurde darüber hinaus die $t(95)$-Grenz zum Ausreißer-Test (12) überschritten, obwohl bei $n = 24$ sogar 1 Wert ν_i mit $t(95) \leqq \tau_i < t(99)$ zulässig wäre. Zur besseren Beurteilung der Qualität der jeweiligen Funktion ist es im vorliegenden Fall zweckmäßig, neben den Fehlergrößen $[s_{\mathrm{c}}]$ und *VK* auch die aus

$$[\mathrm{C}] = F(\overline{\mathrm{I1}}) \text{ bzw. } F(\overline{\mathrm{I2}}) \text{ sowie } [\mathrm{I}] = \mathrm{F}'(C)$$



```
ALCORA ZUSE Z23 MODUS 4


AUSGLEICHSRECHNUNG MIT 2 KONSTANTEN
FLAMMENPHOTOMETRIE FUER C=10 BIS  1 MIKROMOL/CCM



ELEMENT NATRIUM ××××××××××



[11] C[Na]=[A]+[B]×I×I

FUNKTION: Y=[A]×Z1+[B]×Z2

RESULTATE:
    [A]               [B]             [SK]            [SA]             [SB]
 .763342476      .913685427⏨-5    .122033612      .425293711⏨-1    .715266579⏨-7

     •
     •
     •

[14] LN(C[Na]/I)=[A]+[B]×I

FUNKTION: Y=[A]×Z1+[B]×Z2

RESULTATE:
    [A]               [B]             [SK]            [SA]             [SB]
-.546327280⏨1    .834865006⏨-3    .171227787⏨-1   .847439831⏨-2    .122072234⏨-4



ELEMENT KALIUM ×××××××××××.



[21] C[K]=[A]+[B]×I×I

FUNKTION: Y=[A]×Z1+[B]×Z2

RESULTATE:
    [A]               [B]             [SK]            [SA]             [SB]
 .110113248⏨1    .916108420⏨-5    .195601369      .648229159⏨-1    .115072196⏨-6

     •
     •
     •

[24] LN(C[K]/I)=[A]+[B]×I

FUNKTION: Y=[A]×Z1+[B]×Z2

RESULTATE:
    [A]               [B]             [SK]            [SA]             [SB]
-.514240880⏨1    .517558633⏨-3    .333020258⏨-1   .151487100⏨-1    .227399905⏨-4
```

Abb. 6.—Ausschnitt des maschinell erstellten Ergebnis-Bogens.

TABLE IV.—ZUSAMMENSTELLUNG DER RESULTATE (GERUNDET)

Funktion	$C=[A]+[B]\cdot I^2$	$C=[A]\cdot I+[B]\cdot I^2$	$\ln C=[A]+[B]\cdot \ln I$	$\ln \frac{C}{I}=[A]+[B]\cdot I$
		NATRIUM		
Nr.	[11]	[12]	[13]	[14]
[A]	+0,7633	$+2{,}8702\cdot 10^{-3}$	−7,4856	−5,4633
[B]	$+9{,}1369\cdot 10^{-6}$	$+6{,}9065\cdot 10^{-6}$	+1,4041	$+0{,}8349\cdot 10^{-3}$
$[s_K]$	±0,122	±0,168	±0,0669	±0,0171
$[s_A]$	±0,0425	$\pm 0{,}228\cdot 10^{-3}$	±0,151	±0,0085
$[s_B]$	$\pm 0{,}0715\cdot 10^{-6}$	$\pm 0{,}266 . 10^{-6}$	±0,0239	$\pm 0{,}0122\cdot 10^{-3}$
		KALIUM		
Nr.	[21]	[22]	[23]	[24]
[A]	+1,1011	$+4{,}6823\cdot 10^{-3}$	−6,1781	−5,1424
[B]	$+9{,}1611\cdot 10^{-6}$	$+5{,}3020\cdot 10^{-6}$	+1,2164	$+0{,}5176\cdot 10^{-3}$
$[s_K]$	±0,196	±0,131	±0,0708	±0,0333
$[s_A]$	±0,0648	$\pm 0{,}180\cdot 10^{-3}$	±0,137	±0,0151
$[s_B]$	$\pm 0{,}1151\cdot 10^{-6}$	$\pm 0{,}213\cdot 10^{-6}$	±0,0219	±0,0227 · 1 0

Standardabweichungen $[s_c]$ in μMol · cm^{-3} und Variationskoeffizienten *VK*

Na $[s_c]_o$	±0,122	±0,168	±0,669	±0,172
$[s_c]_u$			±0,067	±0,020
VK_o	±1,22 Rel%	±1,68 Rel%	±6,69 Rel%	±1,72 Rel%
VK_u	±12,2 Rel%	±16,8 Rel%		±1,95 Rel%
K $[s_c]_o$	±0,196	±0,131	±0,708	±0,333
$[s_c]_u$			±0,071	±0,035
VK_o	±1,96 Rel%	±1,31 Rel%	±7,08 Rel%	±3,33 Rel%
VK_u	±19,6 Rel%	±13,1 Rel%		±3,54 Rel%

TABELLE V.—IST-WERTE C UND $\overline{I1}$ BZW. $\overline{I2}$ UND FUNKTIONELLE SOLL-WERTE [C] UND [I] IN μMol · cm^{-3} BZW. SKT AN DEN GRENZEN DES MAKRO-ARBEITSBEREICHES

	IST	SOLL	[11]	[12]	[13]	[14]
Na	10,0	$[C_o]$ =	9,891	9,768	8,925	9,761
	1,0	$[C_u]$ =	0,899	0,829	0,912	1,020
	999,50	$[I_o]$ =	1005,4	1013,3	1085,2	1012,7*
	196,25	$[I_u]$ =	161,0	225,8	209,6	199,6*
	IST	SOLL	[21]	[22]	[23]	[24]
K	10,0	$[C_o]$ =	10,103	9,851	9,151	9,676
	1,0	$[C_u]$ =	1,122	0,826	0,926	1,050
	991,25	$[I_o]$ =	985,6	1001,0	1066,3	1013,0*
	150,75	$[I_u]$ =	imaginär	177,8	160,6	157,7*

* Durch iterative Rechnung ermittelt.

folgenden funktionellen Sollwerte an der oberen und unteren Grenze des Makro-Arbeitsbereiches zu betrachten. Tabelle V gibt eine Zusammenstellung der entsprechenden Größen.

Sowohl die *VK*-Werte (Tab. IV) als auch die funktionellen Sollwerte (Tab. V) der Funktionen 1 und 2 zeigen unmittelbar, daß die Daten-Interpretation durch diese Funktionen insbesondere für kleine *C*-Werte sehr unbefriedigend ist. Sie sind als analytische Berechnungsfunktionen ungeeignet.

Obwohl die Funktion 3 das nach der Literatur mögliche Wurzelgesetz in *C* darstellen kann, erweist sie sich als wenig geeignet zur Interpretaion der hier vorliegenden Daten. Sie scheidet ebenfalls als analytische Berechnungsfunktion aus, da Ist- und Sollwerte vor allem an der oberen Grenze des Arbeitsbereiches erheblich voneinander abweichen. Die Wurzelgrößen sind mit $b = [\mathrm{B}] =$ 1,40 bzw. 1,22 sehr viel kleiner als 2 und lassen vermuten, daß die Meßdaten noch im Übergangsgebiet zwischen linearen und gekrümmten Eichkurven liegen.

Bei der Funktion 4 werden bemerkenswert kleine Fehlergrößen $[s_e]$ und *VK* erhalten, wobei auch die Ist- und Sollgrößen an den Bereichsgrenzen relativ gut übereinstimmen. Daher ist der Funktionstyp 4 unter den hier vorgeschriebenen Versuchsbedingungen als analytische Berechnungsfunktion grundsätzlich brauchbar. Die entsprechenden Formeln

für Na: $C = 4{,}2396 \cdot 10^{-3} \cdot I \cdot \mathrm{EXP}\,\{0{,}83487 \cdot 10^{-3} \cdot I\}$

oder $\log C = \log I + 0{,}362577 \cdot 10^{-3} \cdot I - 2{,}372669$

für K: $C = 5{,}8446 \cdot 10^{-3} \cdot I \cdot \mathrm{EXP}\,\{0{,}517559 \cdot 10^{-3} \cdot I\}$

oder $\log C = \log I + 0{,}224773 \cdot 10^{-3} \cdot I - 2{,}333320$

sind jedoch kompliziert. Sofern man Messungen im Makro-Arbeitsbereich nicht ohnehin durch Verdünnung der Probelösung vermeidet, wird der zu einem Meßwert *I* gehörende *C*-Wert zweckmäßig direkt einer Eichkurve entnommen.

Das Konzentrationsgesetz $C = a \cdot I \cdot e^{b \cdot I}$ ist ein empirisches Gesetz, von dem sich lediglich sagen läßt, daß die Konstante *a* mit wachsenden Effekten der Selbstabsorption und Selbstumkehr kleiner, die Konstante *b* jedoch größer wird. Im gleichen Konzentrationsbereich sind diese Effekte bei Natrium stärker als bei Kalium.

Summary—Optimal functions to interpret the relationship between different series of experimental data measured for similar objects or processes can be found by least squares adjustments of systematically varied functions. The mathematical structure of a universally applicable equation with two constants has been developed, and also two reduced equations with only one constant each. A calculation procedure, named AUSGL 2, is given for it in the problem-oriented language ALGOL for electronic computing. This procedure is a cybernetic "black box" and is used as a closed block within a simple frame programme for special problems. Its practical use presupposes only a little mathematical knowledge. By means of briefly outlined examples of the application of the function to bi-, ter- and multivalent adjustment of corresponding series of analytical results, a partially novel approach to a rational test and evaluation technique is shown. In a comprehensive example a functional analysis is made of two flame-photometric test series for Na and K in concentration ranges which result—through self-absorption and self-reversal—in non-linear calibration curves. By a simple frame programme a total of 8 (2 × 4) functions can be electronically evaluated in less than 17 min, whereas the time needed for conventional calculation is more than 170 times as long.

Résumé—On peut trouver les fonctions optimales pour interpréter la relation entre différentes séries de données mesurées pour des objets ou procédés similaires par égalisation de fonctions variant systématiquement par la méthode des moindres carrés. On a développé la structure mathématique d'une équation universellement applicable avec deux constantes, et aussi deux équations réduites avec seulement une constante chacune. On donne pour cela un procédé de calcul, appelé AUSGL 2 dans le langage ALGOL pour la computation électronique. Ce procédé est une "boitre noire" cybernétique et est utilisé comme un bloc clos à l'intérieur d'un programme-cadre simple pour des problèmes spéciaux. Son emploi pratique ne présuppose que peu de connaissances mathématiques. Au moyen d'exemples brièvement esquissés de l'application de la fonction à l'égalisation bi-, ter- et multivalente de série correpondantes de résultats analytiques, on montre une approche partiellement nouvelle d'un essai rationnel et d'une technique d'évaluation. Dans un exemple complet, on effectue l'analyse fonctionnelle de deux séries d'essais de photométrie de flamme pour Na et K dans des domaines de concentration menant—par auto-absorption et auto-renversement—à des courbes d'étalonnage non linéaires. Par un simple programme-cadre, on peut évaluer un total de 8 (2 × 4) fonctions électroniquement en moins de 17 min, alors que le temps nécessité par le calcul ordinaire est plus de 170 fois plus long.

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POLAROGRAPHIC REDUCTION BEHAVIOUR OF CLAY MINERALS

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Summary—Suspensions of the clay minerals bentonite, kaolinite illite and chlorite have been examined polarographically and reduction waves found. The differences in their behaviour, with and without the addition of surface active reagents, are reported.

THE accidental discovery by Micka[1] of the polarographic reduction of insoluble substances at the dropping mercury electrode (D.M.E.) has already been confirmed by Hallum and Drushel's results on Carbon Black suspensions.[2] The most striking and important result of these investigations is that substances of similar chemical composition but of different crystallographic form show different reduction behaviour. Zagorski[3] and Kalvoda,[4] using oscillopolarography, found the colour, surface-area and cation-radius of the insoluble substances which they studied were significant.

The behaviour of clay minerals towards polarographic reduction presents results of great complexity and nothing has so far been reported indicating the utility of such studies on clay suspensions. In this communication is presented a new approach to the identification and characterization of clay minerals on the basis of their polarographic behaviour.

EXPERIMENTAL

Clay minerals

Bentonite, kaolinite and illite were obtained from the Ward's Natural Clay Corporation. Modified chlorite-like minerals were obtained by the transformation of bentonite by the precipitation of hydrous metal oxides [$Mg(OH)_2$, $Ni(OH)_2$, $Fe(OH)_2$, or $Al(OH)_3$] in between the silica sheets of montmorillonite units.[5] The dilute clay suspensions were converted into their hydrogen forms by ion-exchange treatment (Amberlite IR-120), and the particle size was controlled by centrifugation.

Apparatus

Toshniwal's battery-operated manual polarograph type CLO-2 was used with a Pye Scalamp galvanometer. Nitrogen was used for deaeration of solutions. The H-type polarographic cell was maintained at 30 ± 0·01°. The capillary constant $m^{2/3}t^{1/6}$ was 2·985; the drop-time was 3·4 sec (open circuit). A saturated calomel electrode was used as reference.

Supporting electrolyte and maxima suppressors

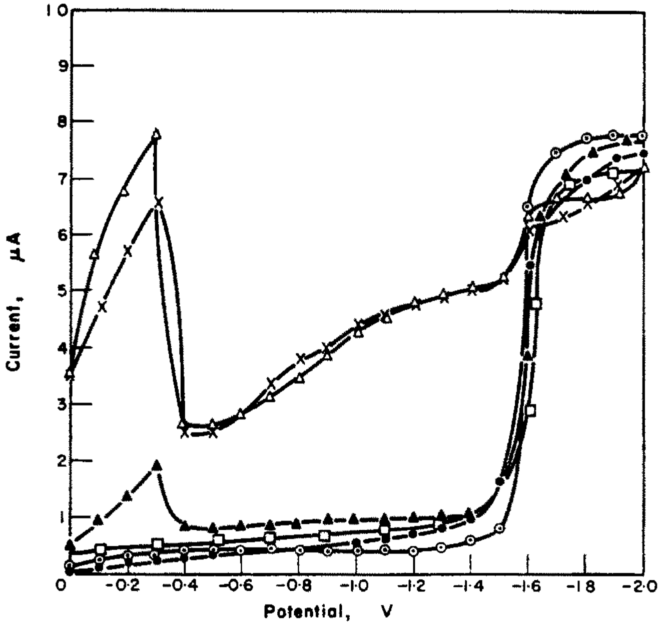
As clay suspensions are known to coagulate in the presence of either charged or uncharged additives,[6] the measurements were made without the addition of any supporting electrolyte, focusing attention mainly on currents other than the diffusion-controlled ones. Solutions, with $10^{-3}M$ concentration of a surfactant such as gelatin, Methyl Red, cationic soap (cetyltrimethylammonium bromide), anionic soap (sulphonated phenylstearic acid) or non-ionic soap (lauric acid–diethanolamine condensate) in doubly distilled water, were used as maxima suppressors.

Preparation of solutions

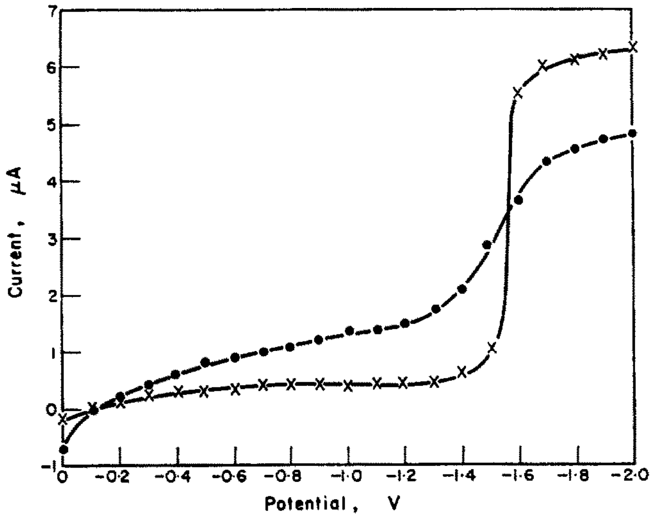
The clay suspension (20 ml) was mixed with the required amount of surfactant and suitably diluted. Solutions were kept in well corked Pyrex tubes for 6 hr to attain equilibrium.

Procedure

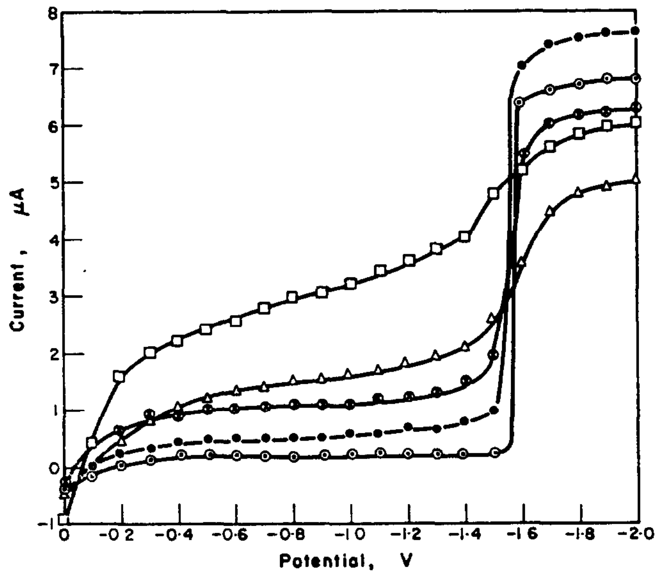
Polarograms were obtained following the usual method.[7] The effect of varying the height of the mercury column and of adding an external resistance was also studied. No anodic waves were found.



(a) Kaolinite—▲—fresh; —□—aged 30 days
Bentonite—●—fresh; —⊙—aged 30 days
Illite—△—fresh; —×—aged 30 days



(b)—×—Soap 2·5 × $10^{-4}M$; —●—soap $10^{-4}M$



(c) Anionic soap—○—2·5 × $10^{-5}M$; —●—$10^{-4}M$ cationic soap—⊗—2·5 × $10^{-5}M$; —△—5 × $10^{-5}M$; —□—$10^{-4}M$

FIG. 1.—Polarographic reduction waves for (*a*) kaolinite, bentonite and illite, showing the effect of aging, (*b*) effect of non-ionic soap on bentonite curves, and (*c*) effect of ionic soap on bentonite curves.

RESULTS AND DISCUSSION

The striking features of the reduction of the various clay minerals at the D.M.E. (Fig. 1a) are (*i*) the appearance of a well defined polarographic reduction wave with $E_{1/2}$ at −1·6 V, (*ii*) the existence of maxima (except in the case of bentonite) at −0·3 V, and (*iii*) the absence of any high migration currents even in the absence of any supporting electrolyte.

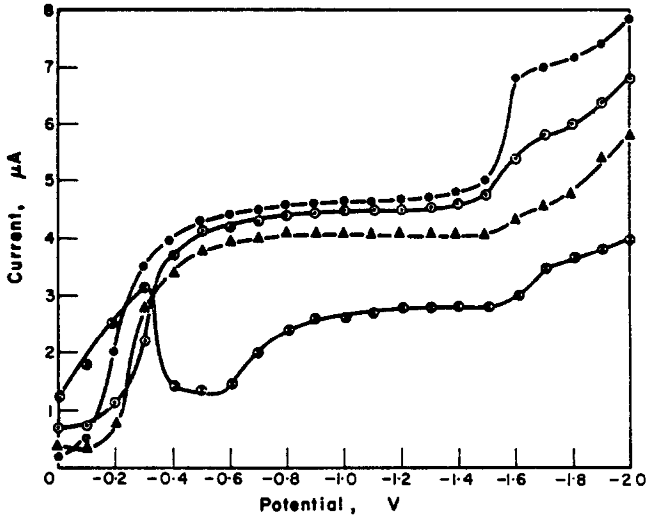
Nature of the reduction wave

The polarographic wave with $E_{1/2}$ at −1·6 V could be the hydrogen wave, but since the $E_{1/2}$ for aluminium also lies near this potential, the possibility of a mixed wave cannot be ruled out. The fact that the height of this wave decreases on aging of the suspension supports this hypothesis. It appears that on aging, replacement of hydrogen ions by aluminium ions takes place, resulting in the lowering of the diffusion current owing to the lower diffusibility of aluminium ions. Since replacement of this type is very small in two-layer clay minerals, very little change in the height of this wave is observed for kaolinite on aging, Fig. 1a.

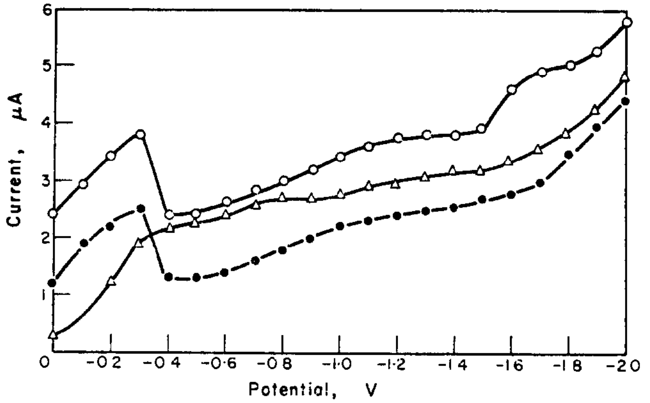
Distortion and disappearance of such waves on the addition of surfactants (except anionic soap) is quite normal.[4] In the case of the anionic soap the height of the wave increases since the soap may also release hydrogen ions which can be reduced, Figs. 1b and 1c.

Nature of the maxima

Except in the case of bentonite, maxima appear at −0·3 V for all the minerals investigated. Though they all appear at the same potential, their behaviour differs from one to the next. Thus for chlorite and illite the maxima remain on aging, whereas for kaolinite they disappear. The maxima are almost or entirely suppressed by the addition of suppressors (surfactants) in the case of kaolinite and illite, and in the latter case, a new wave is formed after the disappearance of the maximum, Fig. 2.



(a) Cationic soap—⊗—5 × $10^{-5}M$; —▲—$10^{-4}M$; anionic soap—○—2·5 × $10^{-5}M$; —●—5 × $10^{-5}M$

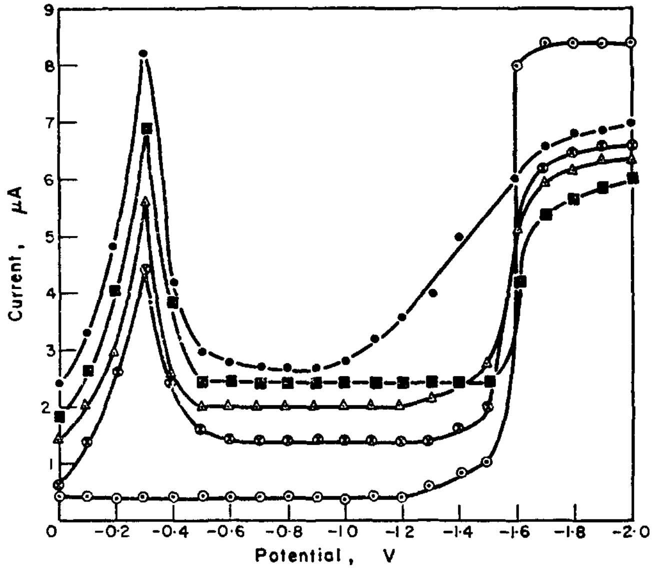


(b) Non-ionic soap—○—$10^{-4}M$; —●—1·5 × $10^{-4}M$; —△—2 × $10^{-4}M$

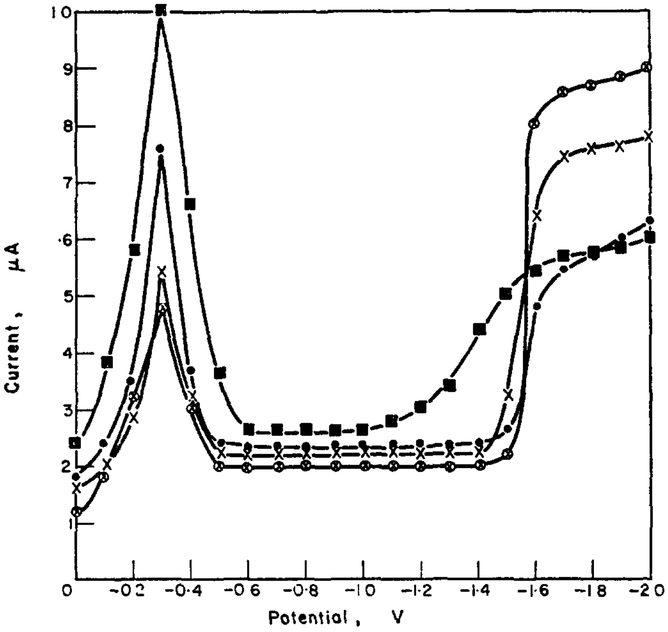
FIG. 2.—Effect of soaps on reduction waves for illite.

With chlorite the behaviour is quite different, the addition of cationic or non-ionic surfactants bringing about an increase in the height of the maxima (though not in proportion to the amount of surfactant added), Fig. 3.

On the basis of these considerations and the fact that these maxima are not those of ordinary polarographic waves, it may be concluded that they are characteristic of the clay minerals, and that their existence depends on the physical state of the particles and on the crystal structures and their previous history. Further evidence



(a) Soap—⊗—1·5 × $10^{-5}M$; —△—3 × $10^{-5}M$; —■—5 × $10^{-5}M$; —●—$10^{-4}M$; effect of resistance—⊙—



(b) Soap—×—1·5 × $10^{-5}M$; —⊗—3 × $10^{-5}M$; —●—5 × $10^{-5}M$; —■—$10^{-4}M$

FIG. 3.—Effect of (*a*) non-ionic soaps and resistance, (*b*) cationic soap on reduction waves for magnesium-chlorite.

that these maxima do not form a part of the normal diffusion current is that the insertion of a high resistance in series with the cell leads to their disappearance, in agreement with the earlier observations of Brdička[8] who found that prominent maxima are strongly suppressed by such an arrangement.

Origin of the maxima

When some form of polarographically active substance is adsorbed at the D.M.E. two waves are obtained, one for the free form, and the other for the adsorbed form.[7] It seems that in these cases the maxima are due to the adsorption of the clay particles on the mercury drops and the second wave is due to the reduction of hydrogen ions or aluminium ions (or both).

Aging of the sol can bring about agglomeration of the particles, thereby reducing their surface-active properties which would subsequently result in lesser adsorption of the particles on the D.M.E. Complete disappearance or decrease in the height of these maxima on aging could be due to this.

Addition of surfactants would considerably reduce the adsorption of clay particles on the D.M.E. thus reducing the adsorption current, resulting in the disappearance of the maxima. That no maximum appears in the presence of anionic soap, even for chlorite, suggests that the mercury drop is positively charged, which is quite probable if we assume that the hydrogen–clay complex dissociates as follows:

$$\text{H–clay} \rightarrow \text{H}^+ + \text{clay}^-$$

The clay anion will now be adsorbed on the mercury drop and with the flow of electrons in the inner mercury layer the mercury surface will eventually become positively charged. The diffusion of anionic soap will now be very much accelerated towards the positively charged mercury surface and the clay anions will get very little opportunity to be adsorbed on the mercury drops, so that a maximum will not appear. Moreover, since the maximum appears at a less negative potential (—0·3 V) than the electrocapillary maximum (—0·56 V) the adsorption of the anions of the soap will be further promoted.

Behaviour of chlorite

An interesting behaviour is observed with the artificially prepared chlorite mineral from bentonite and hydrous metal oxide. Neither bentonite nor the hydrous metal oxides show any maxima in their polarograms, and the appearance of a maximum,

TABLE I.—POLAROGRAPHIC BEHAVIOUR OF SUSPENSIONS OF CLAY MINERALS

Mineral	Maximum, *V*	Effect on the maximum of	
		addition of surfactant	aging
Bentonite	none	—	—
Kaolinite	—0·3	vanishes	vanishes
Illite	—0·3	vanishes, but wave appears	persists
Chlorite	—0·3	increases	persists

All minerals have a wave at —1·6 V; height increased by the addition of anionic soap; decreased by the addition of other surfactants; decreased by aging.

accompanied by an increase in its height on the addition of maximum suppressors confirms the transformation of the bentonite structure. It is also possible that surfactants, instead of checking the adsorption of clay minerals, are adsorbed on the clay particles themselves and are subsequently reduced, resulting in an enhancement of the current.

From this work, it seems that polarographic reduction of clay minerals might be usefully employed for their identification. The results are summarized in Table I.

Zusammenfassung—Suspensionen der Tonmineralien Bentonit, Kaolinit, Illit und Chlorit wurden polarographisch untersucht, und es wurden Reduktionswellen gefunden. Die Unterschiede im Verhalten mit und ohne Zusatz oberflächenaktiver Reagentien werden mitgeteilt.

Résumé—On a examiné polarographiquement des suspensions des minerais argileux bentonite, kaolinite, illite et chlorite, et on a trouvé des vagues de réduction. On décrit les différences dans leur comportement, avec et sans l'addition de réactifs tensioactifs.

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GRAVIMETRIC AND SPECTROPHOTOMETRIC DETERMINATION OF HEXAFLUOROANTIMONATE WITH TETRAPHENYLARSONIUM CHLORIDE, NITRON AND FERROIN

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Summary—Two methods are described for the gravimetric determination of the hexafluoroantimonate anion with tetraphenylarsonium chloride and nitron as precipitants. In addition, a spectrophotometric method for this anion with ferroin as reagent is described. Hydrolysis of the anion is avoided by using stock solutions of $KSbF_6$ in *N,N*-dimethylformamide and adding these directly to concentrated aqueous solutions of the analytical reagent. Interference studies are included on a number of anions.

HEXAFLUOROANTIMONATE is one fluoride complex anion for which, heretofore, there were no direct analytical methods. This is due, in large part, to the instability of the anion with respect to hydrolysis. Lange and Askitopoulos[1] found that this anion was much more easily hydrolysed than the other hexafluoride anions of Group VA. They postulated a stepwise hydrolysis proceeding through ions of the type $SbF_{6-n}(OH)_n^-$. With a paper chromatographic technique with antimony-124 as tracer, Kolditz and Sarrach[2] were able to identify ions of this type for which $n = 1$–4. They reported that the SbF_5OH^- ion was the principal anionic species present in aqueous $KSbF_6$ solutions and that the SbF_6^- ion was present only if the solvent was 40% hydrofluoric acid. Mazeika and Neumann[3] followed the extent of hydrolysis by titration of the fluoride ion produced. They stated that the first step of hydrolysis, resulting in loss of the first fluoride ion, took place very rapidly, at some time between dissolution of the hexafluoroantimonate salt and before the first aliquot could be determined.

Although the hexafluoroantimonate ion differs greatly in hydrolytic stability from the hexafluoroarsenate and hexafluorophosphate anions, Lange and Askitopoulos[1] found that the sparingly soluble salts of the latter two corresponded to sparingly soluble salts of the former anion. They did note, however, that the molar solubilities of corresponding salts increased as the atomic weight of the central atom in the complex increased. Lange and Müller[4] reported that nitron (4,5-dihydro-1,4-diphenyl-3,5-phenylimino-1,2,4-triazole) acetate solutions produced precipitates suitable for gravimetric determinations with the Group VA hexafluoride anions, but these investigators did not carry out the development of systematic analytical methods using this reagent. Tetraphenylarsonium chloride was later found to form insoluble precipitates with both hexafluoroarsenate and hexafluorophosphate. Dess[5] described a gravimetric method for the hexafluoroarsenate ion with this reagent. He also

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mentioned using nitron as a reagent for this anion, but indicated that the tetraphenylarsonium salt had more desirable physical properties as a gravimetric precipitate. In 1963, Affsprung and Archer developed both a gravimetric[6] and an amperometric titration method[7] for the hexafluorophosphate ion, using tetraphenylarsonium chloride as a precipitant.

Because the other two Group VA hexafluoride complexes mentioned gave analytically useful precipitates with both nitron and tetraphenylarsonium chloride, it was decided to attempt the development of two distinct gravimetric methods for the hexafluoroantimonate ion, using these reagents. The two gravimetric methods would then provide a check upon each other. The work described in this paper shows that pure precipitates are obtained and that the two methods give quite comparable results.

In addition to the development of these gravimetric methods, a spectrophotometric method was developed with ferroin [iron(II) 1,10-phenanthroline sulphate] as reagent. Ferroin has been used previously as a spectrophotometric reagent for the hexafluorophosphate[8] and hexafluoroarsenate[9] anions. It was found that these anions were extracted as the iron(II) 1,10-phenanthroline salt into n-butyronitrile, while many other salts of this cation were not extracted. It was found that the hexafluoroantimonate salt of this complex cation was also strongly extracted into n-butyronitrile, which facilitated the development of a quite convenient spectrophotometric method for this fluoride complex.

EXPERIMENTAL

Reagents

Tetraphenylarsonium chloride, 0·10*M aqueous solution*. Filter to remove impurities.

Nitron acetate solutions, 10% *nitron in* 10% *acetic acid*. Prepare just before use in each determination.

Potassium hexafluoroantimonate solutions. Dissolve a 3–5 g sample of high purity* in 100 ml of spectral grade DMF (*N,N*-dimethylformamide) which has been dried over molecular sieves for at least 24 hr.

Ferroin, 0·01*M*. Prepared from iron(II) sulphate and 1,10-phenanthroline.

Tetraphenylarsonium chloride. G. F. Smith Chemical Co.

Nitron. Eastman Organic Chemicals.

Procedures

Gravimetric nitron method. A 3-ml aliquot of solution containing from 0·1000 to 0·1500 g of $KSbF_6$ in DMF is added to a solution containing 5 ml of 10% nitron acetate and 50 ml of 10% acetic acid. This order of addition must be strictly followed to prevent hydrolysis of SbF_6^-. The precipitate is allowed to stand for 15 min at room temperature in contact with the mother liquor. If longer standing times are used, the solutions should be cooled in an ice bath. The precipitate is filtered off on a tared medium-porosity sintered-glass crucible and washed with three or more 10-ml portions of 10% acetic acid solution saturated with nitron hexafluoroantimonate. The precipitate is dried to constant weight at 110° and weighed as $C_{20}H_{16}N_4HSbF_6$.

Gravimetric tetraphenylarsonium chloride method. A 1–3 ml aliquot of solution containing 0·0500 to 0·1000 g of $KSbF_6$ in DMF is added to a solution containing a two-fold molar excess of 0·10*M* tetraphenylarsonium chloride, followed by addition of 20–40 ml of 5–8*M* aqueous ammonia. It is important to keep the water to DMF ratio relatively constant at this point. DMF to water ratios of 1:15 and 1:25 v/v were both found to give good results. Again the given order of addition should be carefully followed. The precipitate is allowed to stand at room temperature for 15–60 min or until flocculated. If longer standing times are required, the solutions should be cooled in an ice-bath to prevent hydrolysis. The precipitate is filtered off on a tared medium-porosity sintered-glass crucible and washed with two or three 25-ml portions of 0·03*M* aqueous ammonia. The precipitate is then dried to constant weight at 110° and weighed as $(C_6H_5)_4AsSbF_6$.

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* Our samples were donated by the Ozark Mahoning Co., Tulsa, Oklahoma.

Spectrophotometric method. Add 1 ml of ferroin, 4 ml of water and 5 ml of n-butyronitrile to a 15-ml glass-stoppered centrifuge tube. To this mixture add 1·000 ml of DMF containing from 2×10^{-4} to 7×10^{-3} mmole of $KSbF_6$. Shake for 30 sec and centrifuge for 2 mm to separate the less dense n-butyronitrile layer from the aqueous layer. Take a 1-ml aliquot of the organic layer and dilute to volume with n-butyronitrile in a 5-ml volumetric flask. Measure the transmittance of the last solution against pure n-butyronitrile at 506 mμ with a 0·10-mm slitwidth, within 10–15 min after beginning the extraction.

Development of the gravimetric methods

Solubility study. Affsprung and Archer[6] found the spectra of tetraphenylarsonium chloride and tetraphenylarsonium hexafluorophosphate to be the same in aqueous solution between 200 and 300 mμ. They utilized an absorption shoulder at 220 mμ with a molar absorptivity of $35{\cdot}7 \times 10^3$ l mole^{-1} cm^{-1} (standard deviation of $0{\cdot}22 \times 10^3$ l mole^{-1} cm^{-1}) in order to determine the molar solubility of the tetraphenylarsonium hexafluorophosphate precipitate. The spectra, in aqueous solution, of tetraphenylarsonium chloride and tetraphenylarsonium hexafluoroantimonate were also found to be identical in this region. However, this spectrophotometric technique could not be used for determination of the solubility of the hexafluoroantimonate salt in water–DMF mixtures because of ultraviolet absorption by DMF. Therefore, the solubility of tetraphenylarsonium hexafluoroantimonate was determined in distilled water by the following technique. Saturated water solutions were prepared from freshly precipitated $(C_6H_5)_4AsSbF_6$ and equilibrated by frequent shaking for 1–2 hr at 25°. The absorbance of the solutions was then measured at 220 mμ and the mean concentration was found to be $2{\cdot}4 \times 10^{-4}M$.

Lange and Askitopoulos[1] found that the solubility of nitron hexafluoroantimonate in water was $6 \times 10^{-3}M$. This is too soluble a precipitate to be used in a normal, straightforward gravimetric procedure; however, it was assumed that if the wash solution was first saturated with the precipitate, very little precipitate would be lost in the washing operation and that the analytical results obtained would be meaningful.

Precipitate composition. Since Kolditz and Sarrach[3] had indicated that nitron pentafluoromonohydroxoantimonate(V) dihydrate was precipitated from aqueous $KSbF_6$ solutions, a great amount of evidence was necessary in order to prove that the precipitates obtained were actually the hexafluoroantimonate salts. Therefore both the tetraphenylarsonium hexafluoroantimonate and the nitron hexafluoroantimonate precipitates were subjected to elemental analysis to confirm their compositions. In addition, the pentafluoromonohydroxoantimonate(V) salts of both nitron and the tetraphenylarsonium ion were prepared, and their infrared spectra were compared with those of the precipitates obtained in the gravimetric analyses.

Nitron pentafluoromonohydroxoantimonate(V) and tetraphenylarsonium pentafluoromonohydroxoantimonate(V) were prepared by dissolving a few grams of $KSbF_6$ in water and allowing the solution to stand for 15 min before pouring it into either a 10% nitron acetate solution or a 0·10*M* tetraphenylarsonium chloride solution. The compounds precipitated readily with apparently good yield; however, the tetraphenylarsonium compound seemed to redissolve rapidly. The nitron salt was filtered off and vigorously washed with 10% acetic acid, after which part of it was air-dried and part of it was dried overnight at 130°. The tetraphenylarsonium compound was filtered off, washed with 5 ml of 0·03*M* aqueous ammonia and dried overnight at 130°.

Infrared spectra were taken of nitron, tetraphenylarsonium chloride, $KSbF_6$, the gravimetric precipitates [$C_{20}H_{16}N_4HSbF_6$ and $(C_6H_5)_4AsSbF_6$], and the corresponding monohydroxy compounds of the precipitates. The infrared spectra were scanned over the region from 4000 cm^{-1} to 250 cm^{-1} with a Beckman IR-10 spectrophotometer. The compounds were prepared as mulls in Nujol and run on caesium bromide plates.

Interference study on the gravimetric methods. Any anion which forms a precipitate with nitron or tetraphenylarsonium chloride will interfere. Typical anions of this type are permanganate, perrhenate, perchlorate, bromide, iodide, difluorophosphate, hexafluorophosphate, and hexafluoroarsenate. The most likely contaminating anions occurring in hexafluoroantimonate salts are the hydrolysis products: anions of the type $SbF_{6-n}(OH)_n^-$, and fluoride.

Alkali metal salts of fluoride were found to have a relatively low solubility in DMF. The solubility of potassium fluoride was determined in DMF by a direct gravimetric method and found to be 0·16 mg/ml. In addition, qualitative tests on sodium fluoride indicated a very low solubility in DMF. Therefore, regardless of the amount of potassium fluoride in a sample, very little would be transferred to the aqueous solution during the precipitation. Fluoride interference checks were made on both gravimetric methods, using DMF solutions of potassium hexafluoroantimonate saturated with potassium fluoride.

Any interference due to precipitation of the hydrolysis products in the aqueous ammonia–DMF precipitation medium is felt to be negligible or non-existent. Ten ml of an aqueous solution containing about 3 millimoles of $KSbF_6$ were added to 5 ml of concentrated aqueous ammonia. Six ml of 0·09*M* tetraphenylarsonium chloride were added immediately and no precipitate formed. This would seem to indicate that in 5*M* aqueous ammonia the hydrolysis is so complete that no anionic species are present which form insoluble salts with tetraphenylarsonium ion. This fast hydrolysis is the principal reason for the addition of $KSbF_6$ solution in DMF directly to the precipitating reagent.

Development of the spectrophotometric method

pH Study. The effect of the pH of the aqueous solution on the method was studied, using several buffer solutions in the pH range 2·2–10·6. The pH of the solutions was measured on a Beckman Model 72 pH meter. The studies were made by taking 4 ml of the buffer solution, 1 ml of ferroin, and 5 ml of n-butyronitrile. One ml of $1{\cdot}267 \times 10^{-3}M$ $KSbF_6$ in DMF was added, after which the extraction was performed and transmittance measurements were made as usual.

Anion interference studies. A series of anions was checked for possible interference in the following manner: 1 ml of a 0·2*M* solution of a sodium, potassium or ammonium salt of the anion was added to 3 ml of water, 1 ml of ferroin, and 5 ml of n-butyronitrile, after which 1 ml of a solution of $KSbF_6$ in DMF was added. The usual procedure was then followed.

Several common salts were checked for interference at a series of higher concentrations. The salts checked were NH_4Cl, NaCl, $NH_4C_2H_3O_2$, $NaC_2H_3O_2$, Na_2SO_4, and KF.

Stability studies on extracts. Extractions were made on a series of $KSbF_6$ solutions in DMF in the usual manner. The absorbances of the extracts were then measured as a function of time over a 20-hr period.

RESULTS, DISCUSSION, AND CONCLUSIONS

The analytical results obtained on the $KSbF_6$ sample by both the tetraphenylarsonium chloride method and the nitron method were quite comparable and reasonably precise. Thirty-seven determinations were made by the nitron method. The mean $KSbF_6$ found by this method was 100·08% with a standard deviation of 0·44%. Fifty-six determinations were made by the tetraphenylarsonium chloride method. The mean $KSbF_6$ found was 100·45% with a standard deviation of 0·54%.

The precipitates were quite pure and corresponded quite closely to the expected elemental composition as is shown in Table I. The infrared spectra showed conclusively that the gravimetric precipitates were not the hydroxylated fluoroantimonates. The pentafluoromonohydroxoantimonate(V) salt of nitron showed a strong absorption at 3516 cm^{-1} due to the attached OH group. It is interesting to note that the air-dried salt showed the same infrared spectrum as that of the salt dried at 130°. This would seem to indicate that the salt reported as the dihydrate by Kolditz and Sarrach[2] was probably anhydrous nitron pentafluoromonohydroxoantimonate(V). The only other conclusion possible is that the water of hydration is lost under very mild drying conditions indeed. The O—H frequency quoted above corresponds quite closely to the O—H mode reported at 3520 cm^{-1} for this salt by Kolditz and Wendt.[10] The nitron hexafluoroantimonate precipitate obtained from the determinations did not show this peak or any other modes which would indicate the presence of OH groups or water of hydration. The tetraphenylarsonium pentafluoromonohydroxoantimonate(V) salt showed an O—H mode at 3614 cm^{-1}, which was

TABLE I.—ELEMENTAL ANALYSIS OF THE GRAVIMETRIC PRECIPITATES

		C	H	F	N	As	Sb
$(C_6H_5)_4AsSbF_6$	Theoretical, %	46·56	3·26	18·41	—	12·08	19·67
	Experimental, %	46·4	3·4	18·5	—	12·3	19·6
$C_{20}H_{16}N_4HSbF_6$	Theoretical, %	43·74	3·12	20·76	10·20	—	22·17
	Experimental, %	43·8	3·2	20·9	10·0	—	21·9

not present in the infrared spectrum of the tetraphenylarsonium hexafluoroantimonate precipitate. No bands appeared in the infrared spectrum of the tetraphenylarsonium hexafluoroantimonate precipitate which could be attributed to O—H modes.

Certain aspects of the infrared spectra obtained for the various fluoroantimonate salts are worthy of mention at this point. All of the compounds containing the SbF_6^- ion have two very strong absorption bands: one in the region 651–642 cm^{-1} and another in the region 273–268 cm^{-1}. These bands have been tentatively assigned as ν_3 and ν_4, respectively, for Sb-F in these compounds. These assignments are based on an octahedral model and other group theoretical considerations. According to Peacock and Sharp,[11] ν_3 for the SbF_6^- ion occurs at 660 cm^{-1}. Kolditz and Wendt[10] reported slightly higher values for this mode for various alkali metal hexafluoroantimonates. They also noted that ν_3 for these salts decreased with increasing size of the cation. Values obtained by Olah *et al.*[12,13] would seem to place the frequency for this mode between 665 cm^{-1} and 650 cm^{-1}. The values reported in Table II are in line with these previously reported data. It is interesting to note that ν_3 for the monohydroxy analogues of the hexafluoroantimonate salts appears at significantly lower frequencies than ν_3 for the hexafluoroantimonates, as was reported previously by Kolditz and Wendt.[10]

TABLE II.—INFRARED DATA ON SEVERAL FLUOROANTIMONATE SALTS

Compound	Frequency, *cm*$^{-1}$		
	ν_3 Sb-F	ν_4 Sb-F	ν O—H
$KSbF_6$	648 vs; b	268 vs; sh	—
$(C_6H_5)_4AsSbF_6$	651 vs; sh	272 vs; sh	—
$C_{20}H_{16}N_4HSbF_6$	642 vs; sh	273 vs; sh	—
$(C_6H_5)_4AsSbF_5OH$	627 vs; b	274 vs; b	3614 s; b
$C_{20}H_{16}N_4HSbF_5OH$	614 vs; b	271 vs; b	3516 s; b

vs = very strong, s = strong, sh = sharp, b = broad

Fluoride was found not to interfere with either gravimetric method, as is indicated by the data in Table III.

TABLE III.—FLUORIDE INTERFERENCE CHECK ON GRAVIMETRIC METHODS*

	$KSbF_6$, *g*	Precipitate, *g*	$KSbF_6$, %	Mean, %	Std. devn. %
Tetraphenylarsonium chloride method	0·1349	0·3054	100·5	100·1	0·4
	0·1349	0·3049	100·3		
	0·1349	0·3047	100·3		
	0·1349	0·3034	99·9		
	0·1349	0·3023	99·5		
Nitron method	0·1349	0·2653	100·1	100·0	0·4
	0·1349	0·2663	100·4		
	0·1349	0·2635	99·4		
	0·1349	0·2656	100·2		
	0·1349	0·2651	100·0		

* All $KSbF_6$ solutions in DMF saturated with KF.

The spectrophotometric method gives good Beer's law plots over a wide range of $KSbF_6$ concentrations. Based on a least squares analysis of the data, the slope of the calibration line was found to be 240 $mmole^{-1}$ cm^{-1} with a standard deviation of

1·05 $\text{mmole}^{-1}\ \text{cm}^{-1}$. The extracts decolorized rapidly (see Table IV), which necessitated a very rapid extraction and measurement of extract transmittance. This rapid decolorization made an exhaustive extraction impractical, since this procedure required too long a period of time.

Variations in pH between 2·2 and 8·7 did not affect the absorbance of the extracts, but in solutions more alkaline than this the absorbance of the extracts decreased rapidly with increasing pH. This is probably caused by the increasing rate of hydrolysis of the hexafluoroantimonate anion due to basic catalysis.

Results from the anion interference studies on the spectrophotometric method are shown in Table V. Most common anions did not interfere significantly at the 0·20

TABLE IV.—ABSORBANCES OBTAINED FOR INITIAL EXTRACTION AND STABILITY STUDY ON FERROIN EXTRACTS

$KSbF_6$, *μmole*	Absorbance 0 hr	2 hr	4 hr	8 hr	20 hr
0·2534	0·056	0·029	0·011	0·001	0·000
0·5067	0·115	0·089	0·069	0·053	0·032
0·7601	0·178	0·155	0·138	0·130	0·120
1·013	0·229	0·208	0·190	0·181	0·173
1·267	0·294	0·267	0·244	0·227	0·211
1·520	0·354	0·344	0·326	0·314	0·309
1·774	0·420	0·396	0·374	0·356	0·341
2·027	0·469	0·446	0·420	0·392	0·367
2·280	0·541	0·521	0·500	0·488	0·462
2·534	0·597	0·572	0·550	0·535	0·523
3·800	0·925	0·900	0·870	0·851	0·839
5·067	1·208	1·174	1·131	1·097	1·086
6·334	1·509	1·469	1·398	1·377	1·347

TABLE V.—ANION INTERFERENCE STUDIES ON THE SPECTROPHOTOMETRIC METHOD

Salt	Degree of interference
$NH_4C_2H_3O_2$	Slight negative
NH_4Cl	None
NH_4NO_3	Strong positive
K_2CrO_4	None
$K_3Fe(CN)_6$	Moderate negative
KF	None
KIO_3	None
KNO_2	Moderate positive
KSCN	Very strong positive
Na_2HBO_3	None
$NaBO_2$	Slight positive
NaBr	Strong positive
Na_2CO_3	Slight positive
$Na_2C_2O_4$	None
$Na_2H_2IO_6$	Strong negative
Na_3PO_4	Moderate negative
Na_2HPO_4	Slight positive
NaH_2PO_4	None
Na_2PO_3F	None
Na_2SO_4	Slight negative
Na_2SO_3	Moderate positive
$NaKC_4H_4O_6$	None

mmole level. Figure 1 shows the effect of increasing concentrations of various common salts on the extraction method.

In all three of the analytical methods described in this paper the working solutions of $KSbF_6$ were prepared in anhydrous DMF. It was found that these solutions were stable for months when care was taken to exclude water. It was possible in all three cases to develop convenient analytical methods for an anion which is quite hydrolytically unstable, by merely adding a measured volume of the DMF solution to a large excess of the analytical reagent in aqueous medium. Thus an anion which can exist for only very short periods of time in aqueous solution can be quite easily determined merely by use of a certain specific order of addition of reagents.

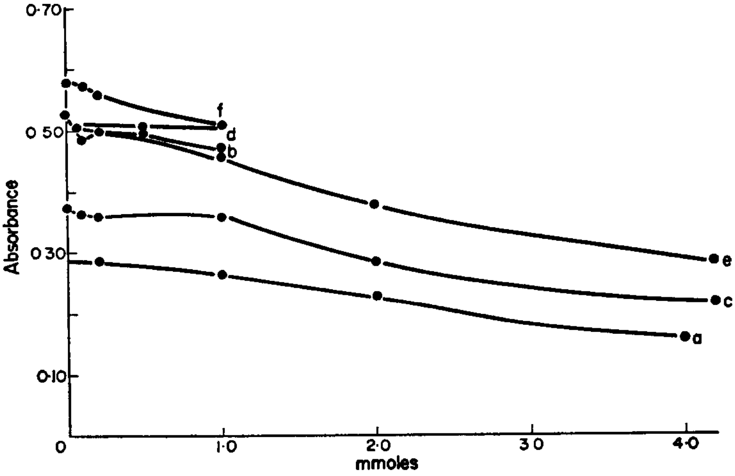

Fig. 1.—Effect of several salts on the spectrophotometric method.

a. KF	*d.* NaCl
b. CH_3COONa	*e.* NH_4Cl
c. CH_3COONH_4	*f.* Na_2SO_4

Zusammenfassung—Zwei Methoden zur gravimetrischen Bestimmung des Hexafluoroantimonat-Anions mit Tetraphenylarsoniumchlorid und Nitron als Fällungsmitteln werden beschrieben. Zusätzlich wird eine spektrophotometrische Methode für dieses Anion mit Ferroin als Reagens beschrieben. Die Hydrolyse des Anions wird vermieden durch Verwendung von Stammlösungen von $KSbF_6$ in N,N-Dimethylformamid und direkte Zugabe zu konzentrierten wäßrigen Lösungen des analytischen Reagens. Störungsuntersuchungen über eine Anzahl von Anionen sind angefügt.

Résumé—On décrit deux méthodes pour le dosage gravimétrique de l'anion hexafluoroantimoniate par le chlorure de tétraphénylarsonium et le nitron comme agents précipitants. En outre, on décrit une méthode spectrophotométrique pour cet anion avec la ferroine comme réactif. On évite l'hydrolyse de l'anion par l'emploi de solutions-stock de $KSbF_6$ en N,N-diméthylformamide et en ajoutant celles-ci directement à des solutions aqueuses concentrées du réactif analytique. On présente des études sur l'interférence d'un certain nombre d'anions.

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POLAROGRAPHIC CURRENTS IN POTASSIUM PEROXYDISULPHATE–ALKALI HALIDE SYSTEMS AND THE DETERMINATION OF PEROXYDISULPHATE ION

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Summary—Potassium peroxydisulphate–alkali halide systems have been studied by d.c. and a.c. (sine wave) polarography. When the mercury drop of the mercury electrode becomes covered by a film of adsorbed bromide or iodide ions, a peak due to peroxydisulphate ion is found in the a.c. polarogram at a potential more negative than that of the halide peak. This peak is probably due to a product of a chemical reaction between the peroxydisulphate ion and halide ion close to the surface of the DME. The determination of the peroxydisulphate ion by a.c. polarography is described.

IT HAS been found that the half-wave potential of the peroxydisulphate electroreduction is shifted to the negative side of the anodic halide wave as soon as the mercury drop is covered by a film of halide ions[1,2] or a film of copper(I) chloride.[3] Halide ions have also been found to produce peaks in a.c. polarography.[4–7] As an overpotential usually causes a system to become less reversible,[8] it was of interest to find out whether the presence of peroxydisulphate in a halide-containing solution is detected in the a.c. polarogram of the halide ion.

EXPERIMENTAL

Reagents

Acetic, perchloric and sulphuric acids, potassium sulphate, potassium hydrogen sulphate, sodium acetate and sodium chloride were guaranteed reagents and sodium iodide an extra pure reagent from E. Merck AG. Sodium bromide was an "Analyzed" reagent from J. T. Baker Chemical Company and sodium perchlorate a B.D.H. laboratory reagent, which was recrystallized from water. A potassium peroxydisulphate solution was prepared daily from the guaranteed reagent from E. Merck AG.

Polarographic method

The polarograms were recorded by the rapid method with a Metrohm E261R Polarograph connected to a Metrohm E393AC-Modulator. The a.c. polarograms were recorded with an a.c. amplitude of 10 mV r.m.s. The height of the mercury head was 60 cm and the characteristics of the DME in an oxygen-free potassium hydrogen sulphate ($0{\cdot}4M$)–sulphuric acid ($0{\cdot}1M$) solution with an open circuit were flow-rate $m = 2{\cdot}43$ mg/sec and drop-time $t = 0{\cdot}16$ sec. Unless otherwise mentioned, the solutions investigated were $0{\cdot}4M$ in potassium hydrogen sulphate and $0{\cdot}1M$ in sulphuric acid, and the temperature was 25°. The solutions were de-aerated with nitrogen for 15 min for the d.c. polarograms, but not for the a.c. polarograms. The reference electrode was an Ag/AgCl/saturated KCl electrode which was connected by a sodium nitrate agar-agar bridge to the polarographic vessel; a tungsten electrode manufactured by Metrohm AG was employed as an auxiliary electrode.

Kinetic runs

Solutions $4 \times 10^{-3}M$ in potassium peroxydisulphate and $8 \times 10^{-3}M$ in sodium iodide the ionic strength (I) of which was adjusted with sodium chloride, were held at 30°. Aliquots (10 ml) of the solutions were taken at intervals and added to 2-ml aliquots of a sulphuric acid ($0{\cdot}1M$)–potassium hydrogen sulphate ($0{\cdot}4M$) solution, and the a.c. polarograms were recorded at 20°.

RESULTS AND DISCUSSION

Currents

When the mercury drop has become covered by a chloride film ($c_{\mathrm{Cl^-}} > c_{\mathrm{crit}}$ where *c* represents concentration), an increase in current is observed at potentials on the negative side of the anodic chloride wave in d.c. polarography when peroxydisulphate ions are present.[8] When an a.c. polarogram is recorded, no peak attributable to peroxydisulphate ion is observed. The effect of peroxydisulphate on the d.c. and a.c. polarograms of the bromide ion and iodide ion is shown by the curves in Figs. 1 and 2,

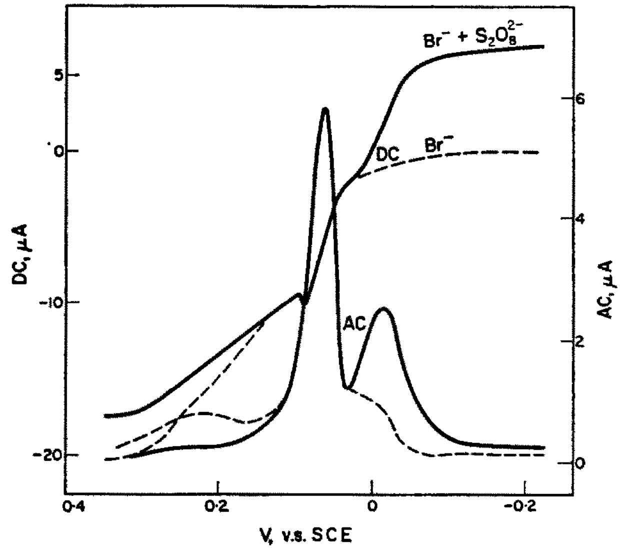

FIG. 1.—Polarograms (d.c. and a.c.) of $4{\cdot}17 \times 10^{-3}M$ bromide solution (dashed line), and a solution $4{\cdot}17 \times 10^{-3}M$ in bromide and $1{\cdot}25 \times 10^{-3}M$ in peroxydisulphate (solid line).

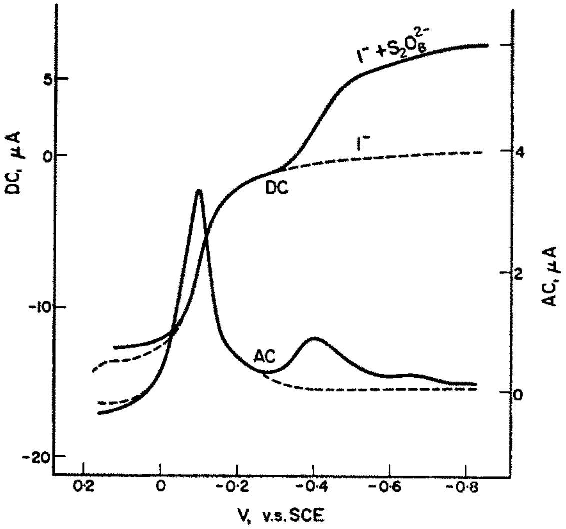

FIG. 2.—Polarograms (d.c. and a.c.) of $4{\cdot}17 \times 10^{-3}M$ iodide solution (dashed line), and a solution $4{\cdot}17 \times 10^{-3}M$ in iodide and $1{\cdot}25 \times 10^{-3}M$ in peroxydisulphate (solid line).

respectively. In both systems the mercury drop becomes covered by a halide film. The polarograms reveal that when the peroxydisulphate ion concentration is increased the a.c. peak due to the bromide ion at the more negative potential increases in height, and in the a.c. polarograms[5,7] of the iodide ion a new peak rises at a potential more negative than the potentials of the iodide peaks. When iodide ion is present, the a.c. current does not fall to the base-current level immediately after this peroxydisulphate peak, but only after the potential is shifted to a value about 0·3 V more negative. This same broad peak is produced also when only peroxydisulphate ion is present in the solution and has been observed previously in a.c. polarograms of the iodide ion.[7] This wave may be due to adsorption of the ions on the mercury surface at potentials more positive than the zero charge potential.

In d.c. polarography the magnitude of the limiting current due to the peroxydisulphate ion on the negative side of the halide wave is nearly independent of the halide ion in solution, although a slight variation is noted. In contrast, the height of the peak in a.c. polarography depends on the halide ion present.

The height of the a.c. peak (Δi_s) caused by peroxydisulphate ion in the presence of bromide ion increases at first with the concentration of the latter ion, but then remains constant (Table I). At high bromide ion concentrations, *i.e.*, when the bromide ion concentration is higher than can be determined by polarography ([Br$^-$] > 8 × $10^{-3}M$), the peak produced by the peroxydisulphate ion decreases in height. A similar variation of the peak height is observed in the presence of iodide ion.

TABLE I.—THE EFFECT OF HALIDE ION CONCENTRATION ON THE HEIGHT OF THE PEROXYDISULPHATE PEAK

[$S_2O_8^{2-}$] $10^{-3}M$	[X^-] $10^{-3}M$	Δi_s, μA Br$^-$	I$^-$
1·25	0·833	0·7	—
1·25	1·25	1·04	0·6
1·25	1·67	1·2	0·68
1·25	2·5	1·5	0·80
1·25	3·33	—	0·78
1·25	4·17	1·5	0·80
1·25	8·33	1·5	0·76
1·25	20·8	1·2	—
4·17	1·67	4·1	—
4·17	4·17	5·2	2·4
4·17	8·33	4·9	—
4·17	12·5	4·4	—

The effects of the peroxydisulphate ion concentration and the temperature are shown in Fig. 3 and Table II. The acidities of concentrated electrolyte solutions and small concentration changes do not essentially alter the a.c. polarography of peroxydisulphate ion in the presence of bromide ion (Table III). Only when the concentration of the supporting electrolyte is reduced considerably does the height of the peak due to peroxydisulphate diminish. At the same time the peak of the bromide ion at the more negative potential increases in height as a consequence of an increase in the capacitance of the double layer surrounding the electrode drop, brought about by increased interaction of the bromide ion with the mercury surface [*cf.* refs. 5 (p. 141) and 6].

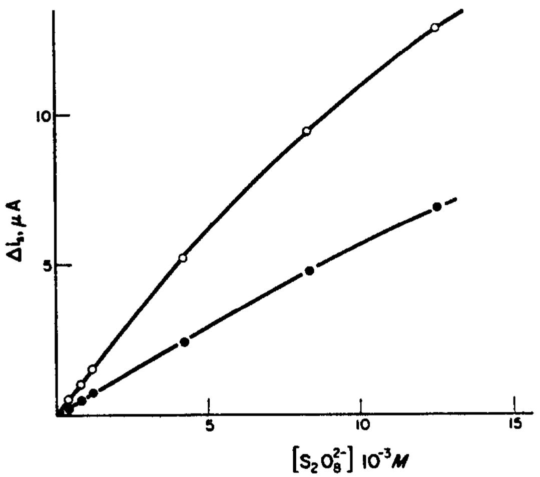

FIG. 3.—The effect of peroxydisulphate concentration on the a.c. peak height. Concentration of halide 4·17 × $10^{-3}M$; o—Br^-; ●—I^-.

TABLE II.—PEROXYDISULPHATE CURRENTS AT VARIOUS TEMPERATURES

Temperature, °*C*	i_{lim}, *μA*	Δi_s, *μA*
0·5	4·5	—
6·5	5·0	0·48
15	6·0	—
20	—	1·3
25	7·1	1·5
35	7·7	—
37	—	1·8
50	9·2	2·3
70	—	2·9

$[S_2O_8^{2-}] = 1·25 \times 10^{-3}M$; $[Br^-] = 4·17 \times 10^{-3}M$.

TABLE III.—THE HEIGHT OF THE PEROXYDISULPHATE (1·25 × $10^{-3}M$) PEAK IN THE PRESENCE OF BROMIDE ION (4·17 × 10*M*) AND DIFFERENT SUPPORTING ELECTROLYTES

Supporting electrolyte	Δi_s, *μA*
0·42*M* $HClO_4$	1·4
0·0833*M* $HClO_4$ + 0·337*M* $NaClO_4$	1·35
0·42*M* $NaClO_4$	1·25
0·0833*M* $NaClO_4$	0·7
0·42*M* K_2SO_4	1·5
0·0833*M* K_2SO_4	1·2

The width of the a.c. peak at half-height cannot be measured when the peroxydisulphate ion concentration is low. When the halide ion concentration is 4·17 × $10^{-3}M$ and the peroxydisulphate ion concentrations are 4·17, 8·33 and 12·5 × $10^{-3}M$, the widths of the peak are 75, 85 and 110 mV, respectively, when the halide is bromide and 170, 180 and 200 mV, respectively, when the ion is iodide.

In d.c. polarography the current caused by the peroxydisulphate ion is a diffusion current. In a.c. polarography the peak attributable to the peroxydisulphate ion is found in the presence of bromide or iodide ion, but not in the presence of chloride ion. Thus, the diffusion of the peroxydisulphate ion cannot be the only reason for the a.c. peak nor can it be due to adsorption or desorption. The data suggest that a reaction takes place between halide and peroxydisulphate ions in the immediate vicinity of the mercury drop and that the peak in a.c. polarography is due to an electrochemical reaction of the product of this reaction. Peroxydisulphate ion reacts much more slowly with bromide than with iodide ion in water,[9] but the peak due to peroxydisulphate is much higher in the presence of bromide ions than in the presence of iodide ions. It should, however, be remembered that the a.c. peaks of bromide ion are higher than those of iodide ion, and that the supposed reaction is taking place at the surface of the mercury drop and thus may be catalysed by mercury. The observed decrease in peak height with increasing halide ion concentration is due to increased interaction of the halide ions and mercury and a consequent small overpotential, which also leads to a slight decrease in the α values in d.c. polarography.

Determination of peroxydisulphate

We can see (Table I and Fig. 3) that the height of the a.c. peak (Δi_s) depends mainly on the peroxydisulphate ion concentration. The peak height is also affected by the concentration and nature of the supporting electrolyte and above all by the halide ion concentration (Table III). Thus in the determination of peroxydisulphate ion the halide ion concentration must lie between about 2 and 10 × $10^{-3}M$.

Several experiments were performed to check the determination of peroxydisulphate ion in the presence of bromide ion. The results of these experiments are shown in Table IV.

TABLE IV.—THE DETERMINATION OF POTASSIUM PEROXYDISULPHATE IN PRESENCE OF POTASSIUM BROMIDE

c_{KBr}	$c_{K_2S_2O_8}$, $10^{-3}M$		Error,
$10^{-3}M$	Taken	Found	%
1·5	1·5	1·35	−10
1·5	6·0	5·8	−3
1·5	12·0	11·7	−2·5
3·3	1·5	1·52	+1
3·3	6·0	6·1	+2
3·3	12·0	11·9	−1
8·0	1·5	1·4	−7
8·0	6·0	6·1	+2
8·0	12·0	11·8	−2

In order to illustrate the determination in the presence of iodide ion, it has been employed in a study of the kinetics of the reaction between peroxydisulphate and iodide ions

$$S_2O_8^{2-} + 2I^- = 2SO_4^{2-} + I_2.$$

As the solution contains iodine after the reaction has begun, the a.c. polarogram is more complicated than without iodine present and the residual current (the peak height with iodine but without peroxydisulphate present) has to be subtracted from the observed peroxydisulphate peak to obtain the true peroxydisulphate peak height.

TABLE V.—THE KINETICS OF THE PEROXYDISULPHATE*–IODINE† REACTION

$\sqrt{I}$	Time, *min*	Peroxydisulphate peak height, μA	k, $10^{-3} l\ mole^{-1} sec^{-1}$
0·14	0	0·725	—
	48	0·67	3·6
	119	0·605	3·5
	174	0·575	3·1
	277	0·505	3·3
	421	0·44	3·2
	645	0·355	3·3
0·20	0	0·81	—
	45	0·735	4·7
	116	0·64	4·8
	170	0·605	4·2
	273	0·53	4·0
	417	0·44	4·2
	641	0·375	3·8
0·40	0	0·945	—
	23	0·88	6·7
	62	0·805	5·8
	130	0·665	6·7
	200	0·58	6·8
	310	0·48	6·5
	420	0·42	6·2
	540	0·375	5·9

* Initial concentration $4{\cdot}0 \times 10^{-3} M$.

† Initial concentration $8{\cdot}0 \times 10^{-3} M$.

The values found are shown in Table V. The values of the rate coefficient were computed from the second-order rate equation

$$k = \frac{1}{2at} \frac{\Delta i_0 - \Delta i_t}{\Delta i_t}$$

where k is the rate coefficient, a the initial peroxydisulphate concentration, t the reaction time in sec, and Δi_0 and Δi_t the peak heights at times 0 and t. (As the rate coefficient depends on the ionic strength, as seen in Table V, and is affected by the tri-iodide formation, the mean values of k are not given.) The calculated values of the rate coefficient are in good agreement with those found previously.[10]

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Résumé—On a étudié les systèmes peroxydisulfate de potassium-halogénure alcalin par polarographie en courant continu et courant alternatif (onde sinusoïdale). Quand la goutte de mercure de l'électrode de mercure se trouve enrobée dans un film d'ions bromure ou iodure adsorbés, on trouve un pic dû à l'ion peroxydisulfate dans le polarogramme en courant alternatif à un potential plus négatif que celui pic de l'halogénure. Ce pic est probablement dû à un produit d'une réaction chimique entre l'ion peroxydisulfate et l'ion halogénure au voisinage de la surface de l'électrode à goutte de mercure. On décrit le dosage de l'ion peroxydisulfate par polarographie en courant alternatif.

Zusammenfassung—Systeme mit Kaliumperoxydisulfat und Alkalihalogeniden wurden gleichstrom- und wechselstrompolarographisch (Sinuswellen) untersucht. Wird der Quecksilbertropfen der Quecksilberelektrode mit einem Film von adsorbierten Bromid- oder Jodidionen

bedeckt, so findet man im Wechselstrompolarogramm bei negativerer Spannung als dem Halogenpeak einen Peak vom Peroxydisulfat. Dieser Peak kommt wahrscheinlich vo, einem Produkt einer chemischen Reaktion zwischen Peroxydisulfation und einen Halogenion in der Nähe der Oberfläche der Quecksilbertropfelektrode. Die wechselstrompolarographische Bestimmung von Kaliumperoxydisulfat wird beschrieben.

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QUANTITATIVE PAPIERCHROMATOGRAPHIE INAKTIVER SUBSTANZEN DURCH RADIOAKTIVE ZUSÄTZE—I

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Zusammenfassung—Es wird eine neue radiometrische Methode zur Bestimmung von inaktivem Sulfat bzw. Thiosulfat auf Papierchromatogrammen beschrieben, die darauf beruht, daß man der zu erfassenden Probe stets die gleiche Menge an Sulfat (^{35}S) bzw. Thiosulfat (^{35}S) zumischt. Für aktive trägerfreie Schwefelsäure wird ein Variationskoeffizient von 4,6% erreicht. Dieser Wert läßt sich durch statistische Auswertung und Computereinsatz auf 3,5% verbessern.

ZUR Bestimmung radioaktiver Substanzen auf Papierchromatogrammen sind schon wiederholt radiometrische Methoden vorgeschlagen worden.[1,2,3] Dabei geht man meistens davon aus, daß die gemessene Aktivität der Substanzmenge des zu bestimmenden Stoffes proportional ist.

$$m = k \cdot I \tag{1}$$

m = Substanzmenge (mg); I = gemessene Gesamtintensität (Imp/min); k = Proportionalitätsfaktor.

Die hohe Präzision der Auswertung radioaktiver Chromatogramme veranlaßte zur Untersuchung der Frage, inwiefern auch inaktive Substanzen radiometrisch analysiert werden können. Hierzu sind bisher zwei Methoden bekannt: Neutronenaktivierungsanalyse,[4] und Umsetzung mit einem radioaktiven Reagens.[5] Die hier dargelegte Methode beruht darauf, variablen Mengen an inaktiver Substanz eine stets gleiche Menge an chemisch gleichartiger, aber aktiver Substanz beizumischen und anschließend zu chromatographieren.

Wird die Gesamtaktivität eines so gebildeten Substanzfleckens schrittweise über einer Schlitzblende der Breite Δx abgetastet, so entsteht bei Darstellung im x–I-Diagramm eine Intensitätsverteilung über die Längsachse des Fleckens (Konzentrationsstufenprofil; Abb. 1a). Bei kontinuierlichem Papiertransport und Verwendung eines Impulsdichtemessers erhält man ein weniger für die mathematische Auswertung geeignetes Impulsdichteprofil (Abb. 1b).

Wird den zu analysierenden inaktiven Substanzen m_1; m_2; m_3; ... stets die gleiche aktive Menge m^* zugemischt, so bleibt unabhängig vom unbekannten m die Gesamtaktivität stets gleich. Beim schrittweisen Ausmessen der Fleckenintensität ist die Δx zugeordnete Stoffmenge proportional der zugehörigen Teilintensität.

$$I_i/I = (m_i + m_i^*)/(m + m^*). \tag{2}$$

Da man eine statistische Verteilung der Menge m^* in der zu bestimmenden inaktiven Menge m mit Sicherheit annehmen kann, ist lediglich die Form des Konzentrationsstufenprofils für die Ermittlung von m als Kenngröße notwendig. Es gilt:

$$I = \sum_1^n I_i \,. \tag{3}$$

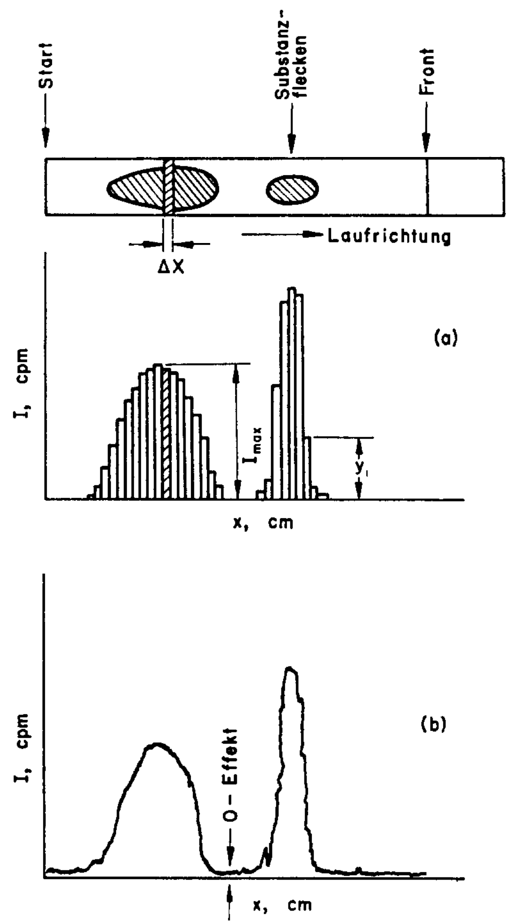

ABB. 1(a).—Schematische Darstellung eines autoradiographierten aktiven Papierchromatogramms und das zugehörige Impuls–Stufenprofil.
(b) Schematisches Impulsdichteprofil analog dem Stufenprofil der (a).

Die absolute Größe von I wird nur bestimmt durch die Vorlage von m^*.

$$I \propto m^*. \tag{4}$$

Fläche unter dem Stufenprofil (Abb. 1a):

$$F = \Delta x \cdot \sum_1^n I_i. \tag{5}$$

Mengenverteilung innerhalb eines Substanzfleckens bei n *Meßschritten*

Wählt man $\Delta x = 1$ und definiert die reduzierten Meßwerte zu

$$y_i = \frac{I_i}{\sum_1^n I_i} \tag{6}$$

so wird die Summe der Teilflächen gleich 1

$$1 = y_1 + y_2 + y_3 + \cdots + y_{n-1} + y_n. \tag{7}$$

Die mathematische Beschreibung des Konzentrationsstufenprofils eines Substanzfleckens führt stets zu einer für x quadratischen Exponentialfunktion.[6] Bei längs der Laufrichtung x normalverteilten Mengen gilt:

$$y = \frac{h}{\sqrt{\pi}} \cdot \exp\left(-h^2 \cdot x^2\right) \tag{8}$$

(statt der Benutzung des in der Statistik üblichen Streuungsparameters σ verwenden wir zur Vereinfachung die Genauigkeitszahl h). Werden die Messungen nach (7) normiert, so ist das Maximum derjenige y_i-Wert, den man der Stelle $x = 0$ zuordnet (gleichbedeutend mit dem Punkt höchster Substanzkonzentration bzw. der maximalen Aktivität $I_{\max}$).

Ist eine Normalverteilung der gesuchten Substanzmenge m innerhalb des Fleckens vorhanden, dann gilt nach erfolgter Normierung der Meßwerte:

$$\frac{h}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \exp\left(-h^2 x^2\right) \mathrm{d}x = 1. \tag{8a}$$

Damit wird die Gaußsche Genauigkeitszahl h eine Funktion der gesuchten Menge m.

$$h = F(m). \tag{9}$$

Die Extrema dieser Beziehung ergeben sich nach:

$$m = 0; \qquad h = +\infty \tag{9a}$$

$$m \rightarrow +\infty; \qquad h \rightarrow 0. \tag{9b}$$

Die präzise Formulierung von (9) ist demnach

$$h = F\left(\frac{1}{m}\right) \tag{10}$$

Da jedoch der aktive Zusatz selbst bei Verwendung von trägerfreiem Material nicht masselos ist (z.B. besitzt 1 mCi $H_2{}^{35}SO_4$ die Masse von 68 ng), kann die Bedingung (9a) praktisch nicht voll erfüllt werden.

Rechnerische Erfassung des Parameters h

Nach Beziehung (8) würde es genügen bei Vorliegen einer reinen Gauß-Funktion den Peak eines Substanzfleckens auszumessen, um den Wert h eindeutig zu bestimmen, denn definitionsgemäß gilt:

$$x = 0; \qquad h = y_{\max} \cdot \sqrt{\pi}. \tag{11}$$

Aus Erfahrung läßt sich sagen, daß mannigfache Unzulänglichkeiten bei der Auswahl der Chromatographiebedingungen (z.B. Fließmittel, Papierqualität, Arbeitsmethodik, Nebeneffekte) zu Deformationen der Flecken führen. Abbildung 2 zeigt zwei solcher Möglichkeiten: (*a*) Schwanzbildung an einem Konzentrationsprofil und (*b*) Deformation eines Konzentrationsprofils.

Bei Vorliegen eines beliebigen nichtidealen Konzentrationsprofils ist es daher wünschenswert, außer dem Wert $y_{\max}$ die gesamte statistische Masse der Meßwerte in die Bestimmung des Parameters h einzubeziehen. Der Weg über die Optimierung der Funktion (8) ist zwar durch die Reihenentwicklung

$$\frac{h}{\sqrt{\pi}} \cdot \exp(-h^2x^2) = \frac{h}{\sqrt{\pi}} \cdot \left(1 - \frac{h^2x^2}{1!} + \frac{h^4x^4}{2!} - \frac{h^6x^6}{3!} + \cdots\right) \tag{12}$$

prinzipiell möglich, erfordert jedoch wegen der zahlreichen Unterprogramme einen elektronischen Großrechner. Es wurde deshalb ein weniger aufwendiger Weg angewandt, der dann seine Berechtigung hat, wenn der Substanzfleck keine Abnormitäten aufweist. Wir verwendeten folgende Vorschrift: Aus der statistischen Masse wählt man 5 Werte, die um das vermutliche Maximum liegen, aus und normiert sie. Abbildung 3 zeigt, daß im Bereich von $y_{\max}$ sich Gauß-Funktion und ausgleichende quadratische Funktion gut decken. Mit Hilfe der 5 ausgewählten Werte gelingt es leicht, die beste Parabel zu finden, deren erste Ableitung das $y_{\max}$ mit guter Genauigkeit liefert. Das Programm der quadratischen Ausgleichsrechnung ist in den meisten Kleinrechenanlagen vorhanden, so daß die Auswertung der Radiopapierchromatogramme auf diese Weise keine Mühe macht.

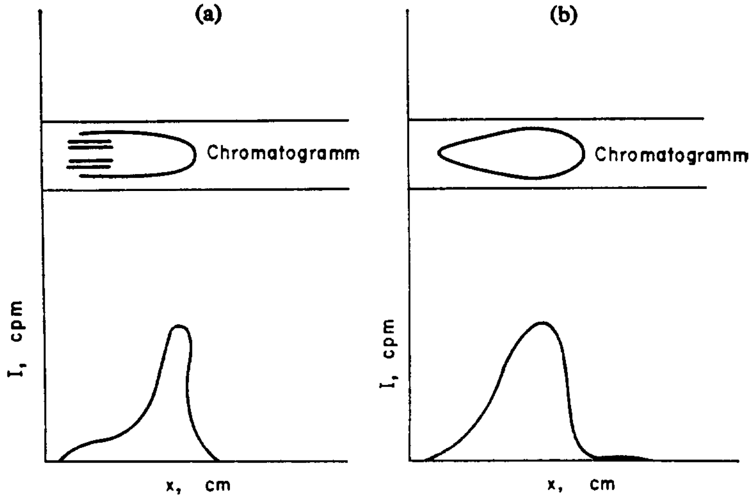

ABB. 2.—Abweichungen von der Glockenform.
(*a*) Substanzfleck läuft zum Startpunkt hin diffus aus.
(*b*) Tropfenförmiger Substanzfleck.

Bei vorgegebenen Eichlösungen m_1; m_2; m_3; ... und den berechneten $y_{\max}$-Werten y_1; y_2; y_3; ... läßt sich eine Eichkurve aufstellen, mit deren Hilfe die graphische Ermittlung der gesuchten Stoffmenge m erfolgt.

EXPERIMENTELLER TEIL

Reagentien

Schwefelsäure (^{35}S) trägerfrei, 1 mCi/ml. Hersteller: Kernforschungszentrum Rossendorf.

Natriumthiosulfat (^{35}S)-*Lösung*, 0,3*M*, 1 mCi/ml. Hersteller: Institut für angewandte Radioaktivität, Leipzig.

Inaktive Schwefelsäure und Natriumthiosulfat-Lösungen (*p.a.*) in je 6 verschiedenen Konzentrationen (siehe Abb. 5 und 6).

Chromatographie

Aufsteigende Methode, Papier FN 8 (Hersteller: VEB Spezialpapierfabrik Niederschlag, Erzgeb.) Zuschnitt 40 × 300 mm. Fließmittel: Pyridin, Isopropanol, Wasser (3:5:5).[7]

Aufgetragene Menge: 2 μl Lösung mittels Chropa-Pipette (Graduierung 0,2 μl); (Hersteller: VEB Glaswerke Ilmenau).

Laufzeit 20 h, Temperatur 20°C (nicht thermostatiert).

Geräte

Meßkontainer VA-H-113; Transportvorrichtung für Papierchromatogramme VA-H-123; Glockenzählrohr VA-Z-320 mit Edelstahlschlitzblende (Spaltbreite 1,5 mm). Zur schrittweisen Auswertung der Chromatogramme benutzten wir den Strahlenmeßplatz VA-M-16D. Hersteller aller genannten Geräte: VEB Vakutronik, Dresden.

Für die Aufnahme der Impulsdichteprofile wurde eine Kombination von Impulsdichtemesser VA-D-41 und Kompensationsbandschreiber verwendet. Hierbei erfolgte der Antrieb von Transportschiene und Registrierpapier synchron mit einer Geschwindigkeit von 6 cm/min. Die mathematische Auswertung erfolgte mit dem elektronischen Kleinrechner SR 2b (Hersteller: VEB Büromaschinenwerke Sömmerda).

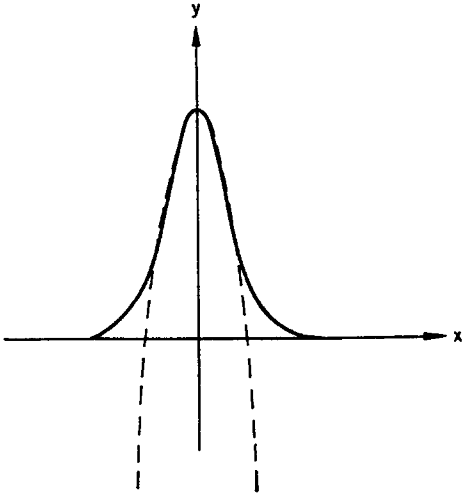

ABB. 3.—Übereinstimmung der Gauß-Funktion (——) mit einer Parabel (- - -) im Bereich innerhalb der Wendepunkte der Glockenkurve.
$h = 0{,}5$; $a = 0{,}04$.

ERGEBNISSE UND DISKUSSION

Um den Nachweis zu führen, daß die Beziehung $h = f(1/c)$ für die quantitative Chromatographie gilt, wurde sowohl für Sulfat- als auch für Thiosulfationen eine derartige radiometrische Analyse durchgeführt. Von 5 verschiedenen inaktiven Sulfatkonzentrationen (0,005, 0,01; 0,02; 0,1; 0,2*N*) entnahmen wir jeweils ein kleines Volumen und vermischten es mit dem gleichen Volumen an aktiver trägerfreir Schwefelsäure. Die mit diesen so markierten Lösungen erhaltenen Chromatogramme wurden durch Autoradiographie sichtbar gemacht (Abb. 4). Als Filmmaterial diente ORWO-RF 44, Exposition 20 h.

Schon geringe Zusätze an inaktiver Schwefelsäure führen zu einer bemerkenswerten Schwanzbildung. Es ist augenscheinlich bereits mittels der autoradiographischen Darstellung möglich, semiquantitative Aussagen über den in den Proben vorhandenen inaktiven Sulfatgehalt zu machen.

Eine bedeutende Steigerung der Aussagegenauigkeit ist jedoch durch registrierende Impulsdichtemessung möglich. Die so gewonnenen Impulsdichteprofile wurden ausgemessen, und die maximale Impulsdichte stellte einen repräsentativen Meßwert für die Menge an inaktivem Sulfat dar. Trägt man das zu jeder Probe gehörende $I_{\max}$ in Abhängigkeit vom vorhandenen inaktiven Sulfatgehalt der jeweiligen Proben auf, so ergibt sich die bereits erläuterte Beziehung (9) in anschaulicher Form.

Da die maximale Peak-Höhe mit dem Gaußschen Genauigkeitsparameter *h* linear zusammenhängt, ist die Abb. 5 eine gültige Eichkurve für die radiometrische Bestimmung inaktiver Sulfatmengen mittels Papierchromatographie. Der in Abb. 5 dargestellte Punkt 1 ist praktisch identisch mit der Konzentration $c_{SO_4^{2-}} = 0$, da die zur trägerfreien aktiven Schwefelsäure gehörende Sulfatkonzentration praktisch unwägbar

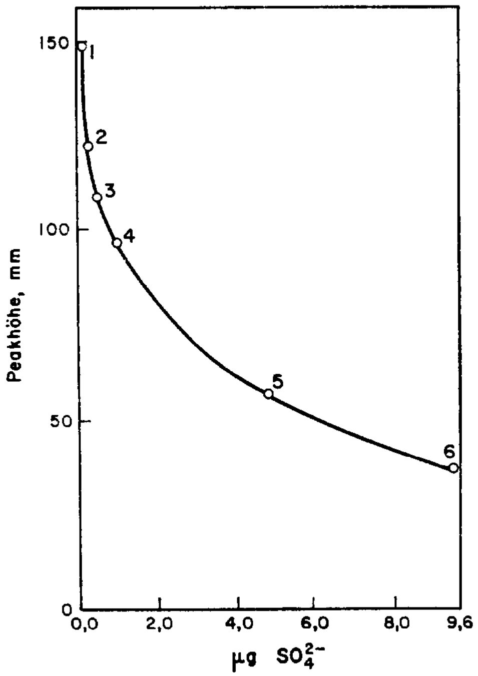

Abb. 5.—Maximale Höhe der Impulsdichteprofile der 6 verwendeten Sulfatkonzentrationen in Abhängigkeit von der aufgetragenen Sulfatmenge.

ist. Vorliegende Methode ist demnach besonders gut für sehr geringe Sulfatgehalte geeignet, da die Steigung der abgebildeten Eichfunktion mit Zunahme an inaktiver Substanz rasch abnimmt. (Gleichbedeutend mit geringeren Meßwertänderungen bei gleichen Konzentrationsintervallen.)

Weitaus ungüngstiger sind die Analysenergebnisse, wenn als radioaktiver Zusatz (Tracer) ein Material verwendet wird, das nicht trägerfrei ist. Wir untersuchten unter den gleichen Chromatographiebedingungen die Impulsdichteprofile von sechs Natriumthiosulfatlösungen. Da die aktive Stammlösung bereits 0,3*M* an Thiosulfat war, mußten die Eichlösungen noch stärker angesetzt werden. Wie die Eichkurve (Abb. 6) zeigt, ist der Funktionsverlauf flacher als bei der Sulfatbestimmung. Da die am Startpunkt aufgetragenen Substanzmengen das für die Papierchromatographie normale Maß bereits überschritten, ergaben die Konzentrationsprofile stark schwankende Flächeninhalte. Es machte sich erforderlich, die Flächen manuell auszumessen und nach Beziehung (2) und (3) eine Reduzierung vorzunehmen. Die

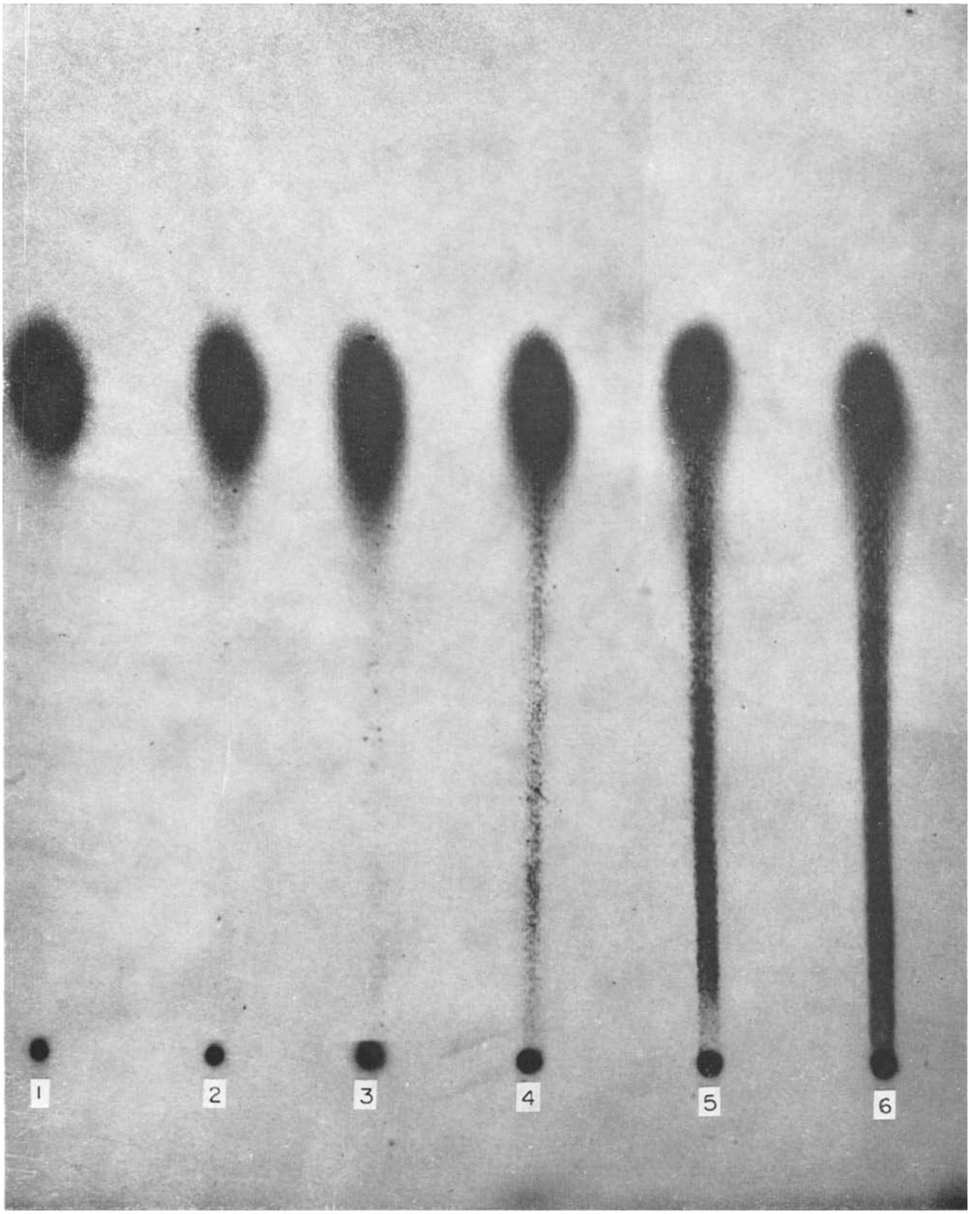

ABB. 4.—Autoradiographie der Chromatogramme von 6 verschiedenen Sulfatkonzentrationen. Aufgetragen wurden je 2 μl mit einer absoluten Aktivität von 2 μCi Startpunkte mit 0,2 μCi nachmarkiert.
1—trägerfreie aktive Schwefelsäure;
2—0,005*N*; *3*—0,01*N*; *4*—0,02*N*; *5*—0,1*N*; *6*—0,2*N*;
(inaktive Schwefelsäure).

Berechnung der reduzierten Peak-Höhen ($I_{\max}/F = y_{\max}$) ergaben die in Abb. 6 dargestellten Werte.

VERFAHRENSBEWERTUNG

Die Genauigkeit, mit der das Arbeitsvolumen von 2 μl auf den Startpunkt gebracht werden kann, beträgt bei Verwendung der Chropa-Pipette etwa 5 %. Werden die erhaltenen Chromatogramme digital und schrittweise radiometrisch ausgewertet, so läßt sich durch Reduzierung der I-Werte der beim Auftragen entstehende Fehler eliminieren. Bei Verwendung der reinen aktiven Schwefelsäure entstehen Chromatogramme mit einem idealen Gauß-Profil. Daher ist dieser Extrempunkt besonders gut zur Demonstration der Reproduzierbarkeit des Analysenverfahrens geeignet (Punkt 1 der Abb. 5). Die Ergebnisse einer solchen Verfahrensbewertung geben jedoch noch nicht Aufschluß über die Güte der gesamten Eichkurve.

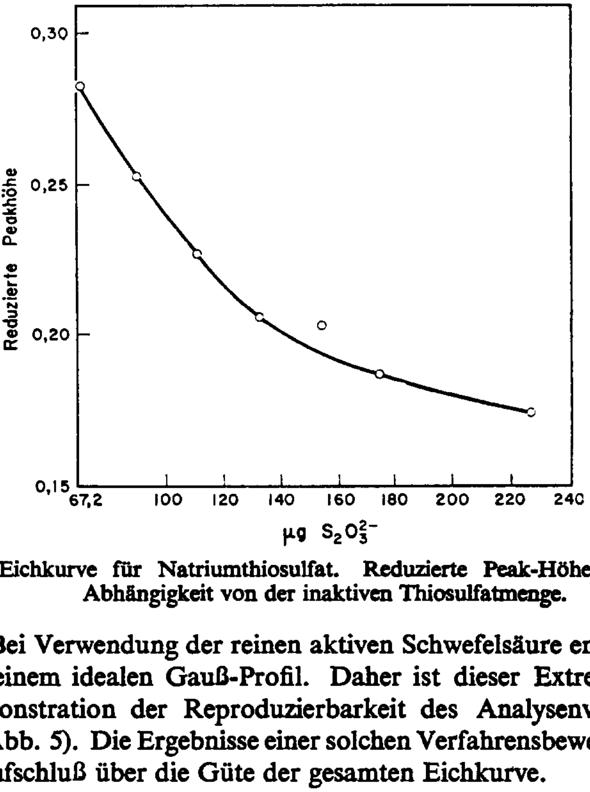

ABB. 6.—Eichkurve für Natriumthiosulfat. Reduzierte Peak-Höhe ($\Sigma y_i = 1$) in Abhängigkeit von der inaktiven Thiosulfatmenge.

Es wurden am Punkt $c = 0$ eine Serie von acht Chromatogrammen angefertigt und diese in ihrer gesamten Ausdehnung mit einer Schlitzblende digital ausgemessen.

TABELLE I.—BERECHNUNG DES VARIATIONSKOEFFIZIENTEN AUS DEN MAXIMALEN IMPULSRATEN DER 8 PROBEN

Lfd. Nr.	$y_{i(\max)}$	$y_i - \bar{y}$	$(y_i - \bar{y})^2$
1	0,183	0,002	4 . 10^{-6}
2	0,199	0,014	196
3	0,177	0,008	64
4	0,185	0,000	0
5	0,193	0,008	64
6	0,186	0,001	1
7	0,172	0,013	169
8	0,183	0,002	4
	$\bar{y} = 0{,}185$	$\Sigma (y_i - \bar{y})^2 = 502 . 10^{-6}$	

TABELLE II.—BERECHNUNG DES VARIATIONSKOEFFIZIENTEN DER 8 PARALLELPROBEN BEI BENUTZUNG VON JEWEILS 5 UM DAS MAXIMUM STREUENDEN IMPULSRATEN

Lfd. Nr.	y_i	a	b	c	d	$y_i - \bar{y}$	$(y_i - \bar{y})^2$
1	0,122 0,164 0,183 0,155 0,130	$1{,}4 . 10^{-3}$	$17{,}5 . 10^{-3}$	0,124	0,177	$6 . 10^{-3}$	$36 . 10^{-6}$
2	0,125 0,164 0,199 0,168 0,104	2,2	24,6	0,127	0,191	8	64
3	0,129 0,171 0,177 0,155 0,109	1,6	17,6	0,130	0,178	5	25
4	0,130 0,173 0,185 0,156 0,115	1,7	18,3	0,131	0,182	1	1
5	0,114 0,157 0,193 0,191 0,143	1,7	24,0	0,109	0,192	9	81
6	0,119 0,161 0,186 0,173 0,115	1,9	22,8	0,116	0,185	2	4
7	0,112 0,158 0,172 0,165 0,128	1,5	19,1	0,112	0,174	9	81
8	0,133 0,178 0,183 0,140 0,081	2,0	19,6	0,135	0,182	1	1

$\bar{y} = 0{,}183$ $\Sigma (y_i - \bar{y})^2 = 293 . 10^{-6}$

y_i = gemessene Impulsraten (reduziert); a, b, c entspricht den Koeffizienten a_1, a_2, a_3, der besten Parabel; d = korrigierter $y_{i(\max)}$-Wert.

Nach Abzug des Untergrundes ergaben sich Glockenkurven, deren Flächeninhalte um den Wert 20 000 ± 1 000 Imp/min. schwankten. Durch Reduzierung gewannen wir vergleichbare y_{max}-Werte, deren Standardabweichungen zu

$$s = \sqrt{\left[\frac{\sum(y_i - \bar{y})^2}{n-1}\right]}$$

definiert ist. Die aus Tabelle I errechnete Standardabweichung beträgt $8{,}5 \,.\, 10^{-3}$; daraus ergibt sich ein Variationskoeffizient von 4,6%. (Der Wert der Standardabweichung ist dimensionslos, da mit reduzierten y-Werten gerechnet wurde.)

Wie bereits erläutert, ist es sehr aufwendig, die Beziehung (11) zur Verbesserung der Varianz des Verfahrens zu benutzen. Es wurden vielmehr zur Berechnung einer besten Parabel je 2 y_i-Werte vor und nach y_{max} in die Berechnung mit einbezogen. Es muß lediglich die Gewähr bestehen, daß die gewählten y_i-Werte nicht in den Bereich der Wendepunkte der Gauß-Funktion fallen.

Die Programmierung wurde so vorgenommen, daß für frei wählbare x-Koordinaten die in Tabelle II, Spalte *a* angegebenen y_i-Werte zu einer besten Parabel verarbeitet werden. In Spalte *b*, *c*, *d* sind die Koeffizienten a_1, a_2, a_3 angegeben. Das Maximum der so gewonnen Funktion $Y = f(x)$ ergibt sich durch eine Differentiation, die im Rechenprogramm enthalten ist. Der neue, ausgeglichene y_{max}-Wert ist in Spalte *d* enthalten.

Die Auswertung der Tabelle II ergibt eine Verbesserung des Variationskoeffizienten des Verfahrens auf 3,5%. Es wurde damit bestätigt, daß eine schrittweise digitale Auswertung der Radiopapierchromatogramme mit anschließender Datenverarbeitung die genauesten Analysenergebnisse liefert.

Es ist beabsichtigt, in einer nachfolgenden Veröffentlichung über die Möglichkeit zu berichten, mittels der hier prinzipiell dargestellten Analysenmethode inaktive Polythionate zu trennen und quantitativ zu analysieren.

Anerkennung—Für die Diskussion und eine Reihe wertvoller Hinweise sind wir Herrn Prof. Dr.-Ing. Gottschalk zu großem Dank verpflichtet.

Summary—A new radiometric method for the determination of inactive sulphate or thiosulphate on paper chromatograms is described, based on the addition, in each determination, of a constant quantity of active sulphate or thiosulphate respectively. For active, carrier-free, sulphuric acid, a relative standard deviation of 4·6% was obtained, but this could be improved to 3·5% by statistical manipulation on a computer.

Résumé—On décrit une nouvelle méthode radiométrique pour la détermination du sulfate ou du thiosulfate inactifs sur chromatogrammes sur papier, basée sur l'addition, dans chaque détermination, d'une quantité constante de sulfate ou de thiosulfate actifs, respectivement. Pour l'acide sulfurique actif, exempt d'entraîneur, on a obtenu un écart type relatif de 4,6%, mais il peut être amélioré à 3,5% par manipulation statistique sur un computeur.

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DETERMINATION OF STRONTIUM IN ENVIRONMENTAL MEDIA

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Summary—A procedure is described for the determination of strontium in natural materials by flame photometry. An alkaline fusion of the ashed sample followed by dissolution in dilute acid gives a preliminary separation. Further separation of strontium is obtained by sorption on Dowex-50 resin from an EDTA solution at pH 5·1 followed by elution of the alkali metals with 0·5*M* hydrochloric acid, and of the strontium with 3*M* hydrochloric acid. The emission line at 460·7 mμ is used and the intensity enhanced by the addition of s-butanol to the solution.

DURING the past two years approximately 400 milk, 200 composite food, 80 vegetation and 30 marine biota and bone samples were analysed in these laboratories for stable strontium. Since a rapid inexpensive method was needed to analyse samples on a mass scale, several procedures were investigated. The involved chemical separations prior to ion-exchange isolation of strontium described by Elfers[1] were eliminated by performing a sodium hydroxide–sodium carbonate fusion.[2] This removed organic matter and soluble carbonates, and provided soluble samples.

At the low concentrations of strontium present in many samples the removal of the interference from large and varying concentrations of calcium became a necessity. A "swamping" technique was investigated but results were too erratic for quantitative analysis. An ion-exchange technique was found to be most suitable for strontium purification.

After dissolution of the carbonate fusion product in hydrochloric acid, the sample was added to EDTA and adjusted to pH 5·1. Over 80% of the calcium was assumed to be complexed by this procedure, since this amount was not adsorbed when the sample solution was passed over cation-exchange resin (Dowex 50W-X8, Na^+ form). Since the resin has a much greater affinity for strontium than for calcium,[3] the residual 18–20% of the calcium was removed with EDTA and dilute acid washes, leaving the strontium adsorbed on the resin.[4] After elution with a stronger acid solution, the strontium was concentrated by evaporation so that it could be determined by flame emission spectrophotometry. An organic solvent was added to increase the intensity of the strontium flame.[5] The chemical yield, which was routinely determined with strontium-85 tracer, ranged from 80 to 95%.

EXPERIMENTAL

Materials

Dowex 50W-X8 (50–100 mesh, Na^+ form) cation-exchange resin (20 ml) in a glass column with coarse fritted disk, 1·9 cm diameter and 30 ml capacity, was prepared by washing with 250 ml of 4*M* sodium chloride followed by 250 ml of distilled water.

Carrier-free strontium-85 tracer was diluted to give approximately 10000 cpm/ml.

EDTA solution, 2%, was prepared by dissolving 22·2 g of the disodium salt in 900 ml of distilled water, adjusting the pH to 5·1 with ammonia solution, and diluting to 1 litre.

Standard strontium solution (1 mg/ml) was prepared by dissolving 1·685 g of strontium carbonate in 0·01*M* hydrochloric acid and diluting to 1 litre.

A Beckman Model DU Spectrophotometer with flame attachment, oxygen–acetylene burner, and IP28 phototube was used for the determinations.

Gamma analyser with 4 in. × 4 in. NaI(Tl) well-crystal.

Procedure

Weigh 5 g of food or milk ash (3 g of vegetation, bone, or marine biota) into a 250-ml nickel crucible. By pipette add 1 ml of strontium-85 tracer to the ash and 1 ml to a counting vial to use as a standard. Mix the ash and tracer thoroughly; add 30 g of sodium hydroxide and mix again. Fuse over a high temperature (Meker) burner until the mixture becomes molten (20–30 min) and then add 3 g of anhydrous sodium carbonate. Heat for 20–30 min more. (Use 20 g of sodium hydroxide and 2 g of anhydrous sodium carbonate for a 3-g sample.) Remove the crucible from the flame and cool it in an ice-bath. Take up the cooled fusion mixture in approximately 200 ml of distilled water and boil gently. Transfer to a 250-ml centrifuge bottle, centrifuge and discard the supernatant liquid. Wash twice with 100-ml portions of hot distilled water. Dissolve the precipitate in 20 ml of 6*M* hydrochloric acid, boiling to expel carbon dioxide, and to aid dissolution. Transfer the solution to a 600-ml beaker containing 300 ml of 2% EDTA solution. Adjust the pH to 5·1 with 6*M* ammonia and dilute to about 450 ml with distilled water which has been adjusted to pH 5·1. Pass the solution through a column containing 20 ml of cation-exchange resin, at a flow-rate of 60–70 ml/min. Wash the column with 500 ml of 2% EDTA solution (pH 5·1) at a flow-rate of 20 ml/min. Elute univalent cations at a flow-rate of 20 ml/min with 500 ml of 0·5*M* hydrochloric acid, and then the strontium at a flow-rate of 10 ml/min with 250 ml of 3*M* hydrochloric acid. Evaporate the eluate to near dryness, add 1 ml of 6*M* hydrochloric acid and transfer to a 50-ml volumetric flask with 20–30 ml of distilled water. Add by pipette 10 ml of s-butanol to the flask, dilute to volume with water, and mix thoroughly.

Transfer 10 ml by pipette into a counting vial to be counted for strontium-85 activity in an NaI(Tl) well-crystal. Compare the counts of the sample with the counts of the standard to determine chemical yield. Determine the strontium by flame photometry at a wavelength of 461 mμ, comparing samples with strontium standards. Prepare solutions for the calibration curve by using appropriate aliquots of the standard solution (1 mg/ml) and adding 20 ml of s-butanol per 100 ml of solution.

A calibration curve ranging from 1 to 15 μg Sr/ml was used for food, milk and most vegetation samples, and a curve from 70 to 120 μg Sr/ml for marine biota and bone samples.

RESULTS AND DISCUSSION

Known amounts of strontium were added to various types of sample and run in conjunction with the original samples. Results showing the accuracy of the procedure for milk and food are given in Tables I and II. Replicate samples of a composite milk ash sample were used to determine the precision; 16 results gave a range of 0·57–0·67 mg of Sr, mean 0·63, relative standard deviation 4·3%.

Organic material and soluble carbonates were removed in the fusion and leaching process and most of the calcium was complexed with EDTA which prevented its adsorption by the cation-exchange resin. Calcium-45 and strontium-85 were used to determine the retention and elution of these elements. Less than 1% of the strontium leaked through while more than 80% of the calcium passed through the cation-exchange column at flow-rates up to 70 ml/min. Virtually all of the remaining calcium was eluted with 2% EDTA. Since sodium and potassium intensify the flame emission of strontium,[6,7] they were separately removed from the column. Their absence in the final sample solution was confirmed flame-photometrically.

Quantitative removal of strontium with 3*M* hydrochloric acid at a flow-rate of 10 ml/min was then accomplished. The elution behaviour of strontium is shown in Fig. 1. Barium was also present in this fraction but did not affect the flame photometric determination of strontium. The small amount of calcium (less than 2%) that

TABLE I.—ACCURACY TEST ON THE RECOVERY OF STRONTIUM FROM MILK ASH (5-g SAMPLES)

Sample no.	Strontium		Differences		
	Added, *mg*	Observed,* *mg*		*mg*	Recovery, %
1	0	0·58	—	—	—
2	1·00	1·63	2 − 1	1·05	105
3	2·00	2·62	3 − 1	2·04	102
4	3·00	3·57	4 − 1	2·99	100
			3 − 2	0·99	99
			4 − 2	1·94	97
			4 − 3	0·95	95
				Mean	99·3
				Std. devn.	3·6

* Includes correction for chemical yield based on tracer ^{85}Sr.

TABLE II.—ACCURACY TEST ON THE RECOVERY OF STRONTIUM FROM FOOD ASH (5-g SAMPLES)

Sample no.	Strontium		Differences		
	Added, *mg*	Observed,* *mg*		*mg*	Recovery, %
1	0	0·70	—	—	—
2	1·00	1·70	2 − 1	1·0	100
3	2·00	2·74	3 − 1	2·04	102
4	3·00	3·66	4 − 1	2·96	99
			3 − 2	1·04	104
			4 − 2	1·96	98
			4 − 3	0·92	92
				Mean	99·1
				Std. devn.	4·1

*Includes correction for chemical yield based on tracer ^{85}Sr.

TABLE III.—EFFECT OF CALCIUM ON EMISSION FROM 10 μg OF STRONTIUM PER ml IN 20% S-BUTANOL MEDIUM

Calcium added, *mg/ml*	0	1	10	50	100
Relative emission	84·5	84·5	88	95	100

TABLE IV.—EFFECT OF ORGANIC SOLVENTS ON EMISSION BY STRONTIUM

Solvent, *v/v*		Relative emission
None		20·5
s-Butanol,	6%	59
	10%	73
	15%	86·5
	20%*	93
n-Butanol	6%*	68
isoButanol	6%*	67

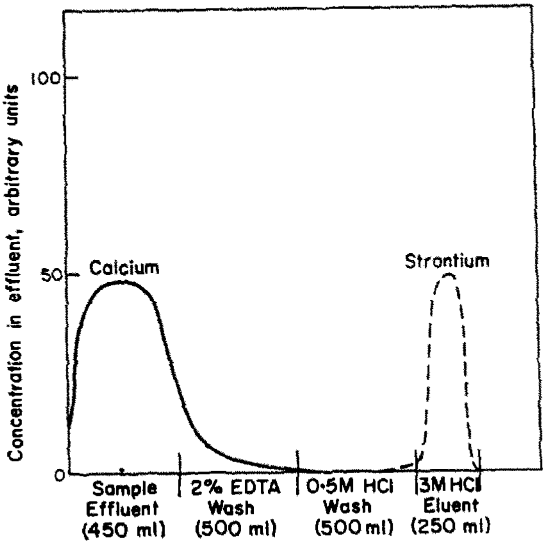

FIG. 1.—Separation of calcium and elution of strontium.

may remain in the sample does not affect the flame emission (see Table III). The effects of several organic solvents on the flame emission of strontium were investigated (see Table IV). s-Butanol, which increased the intensity of the strontium flame more than fourfold, was chosen for use in the routine determination.

The presence of silica in some types of vegetation and biota samples originally caused low yields. This difficulty was overcome by removing most of the silica from the fused sample by precipitation after acidification with 6*M* hydrochloric acid.

After elution of the strontium with 3*M* hydrochloric acid, the resin column may be regenerated for subsequent use by passing 250 ml of 4*M* sodium chloride through the column at a flow-rate of 10 ml/min followed by 200 ml of distilled water.

Acknowledgement—The authors express their appreciation for the professional assistance of C. R. Porter.

Zusammenfassung—Ein flammenphotometrisches Verfahren zur Bestimmung von Strontium in Naturprodukten wird beschrieben. Zur Vorabtrennung wird die veraschte Probe alkalisch geschmolzen und mit verdünnter Säure aufgenommen. Weiter gereingt wird das Strontium durch Adsorption an Dowex-50-Harz aus EDTA-Lösung bei pH 5,1, Elution der Alkalimetalle mit 0,5 M Salzsäure und Elution von Strontium mit 3 *M* Salzsäure. Die Emissionslinie bei 460,7 nm wird benutzt und deren Intensität durch Zugabe von s-Butanol zur Lösung verbessert.

Résumé—On décrit une technique pour le dosage du strontium dans les produits naturels par photométrie de flamme. Une fusion alcaline de l'échantillon inciné suivie de dissolution en acide dilué donne une séparation préliminaire. On obtient une nouvelle séparation du strontium par sorption sur la résine Dowex-50 à partir d'une solution en EDTA de pH 5,1, suivie de l'élution des métaux alcalins par l'acide chlorhydrique 0,5 *M* et du strontium par l'acide chlorhydrique 3 *M*. On utilise la raie d'émission à 460,7 mμ et l'intensité est exaltée par l'addition de *s*-butanol à la solution.

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SPEKTROPHOTOMETRISCHE BESTIMMUNG VON KUPFER MIT 2.3.8.9-DIBENZO-4.7-DIMETHYL-5.6-DIHYDRO-1.10-PHENANTHROLIN (CUPROTEST)

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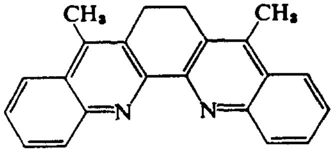
(*Eingegangen* 29 *Mai* 1967. *Angenommen* 21 *Juli* 1967)

Zusammenfassung—Es werden Untersuchungen zur Anwendung von 2.3.8.9-Dibenzo-4.7-dimethyl-5.6-dihydro-1.10-phenanthrolin (Cuprotest) für die photometrische Kupferbestimmung beschrieben. Der Einfluß des pH-Wertes und der Reagenzkonzentration auf den Extraktionsgrad sowie die Anwendbarkeit von 20 verschiedenen organischen Solventien zur Extraktion wurde geprüft. Es zeigte sich, daß man bis zu 50 μg Cu/ml nach Reduktion mittels Ascorbinsäure in Gegenwart von Tartrat-Ionen im pH-Bereich 3–10 mit Cuprotest/Chloroform-Lösung extrahieren und spezifisch bei 554 nm bestimmen kann. Der Einfluß von 60 Kationen und Anionen wurde geprüft. Nur in Gegenwart von ÄDTA, Thiosulfat, Cyanid und Sulfid konnten Störungen festgestellt werden. Das Verfahren wurde zur Untersuchung von 37 Reinststoffen sowie zur Analyse verschiedener technischer und natürlicher Produkte angewandt. Es konnten Nachweisgrenzen bei $8 \cdot 10^{-6}$% und relative Standardabweichungen zwischen 2 und 3% ermittelt werden.

In den letzten Jahren haben zwei Gruppen von Reagenzien wegen ihrer hohen Selektivität für die photometrische Bestimmung von Kupfer ständig an Bedeutung gewonnen: das Oxalyldihydrazid und seine Derivate (Cuprizone) und das 2.2′-Dichinolyl und seine Derivate (Cuproine). Der höheren Empfindlichkeit der Cuprizone steht bei den Cuproinen die Tatsache gegenüber, daß deren Kupferkomplexe mit organischen Lösungsmitteln extrahiert werden können.

Trotz vieler Vorteile haben aber die bisher empfohlenen Verbindungen der zuletzt genannten Reihe [2.2′-Dichinolyl (Cuproin), 2.9-Dimethyl-1.10-phenanthrolin (Neocuproin) und 2.9-Dimethyl-4.7-diphenyl-1.10-phenanthrolin (Bathocuproin)] noch keinen umfassenden Eingang in die analytische Praxis gefunden, da sie infolge ihrer aufwendigen Synthese ziemlich teuer sind.

Nach einem von E. Uhlemann und Mitarb.[2,3,4] vorgeschlagenen Darstellungsverfahren läßt sich als weitere Verbindung dieser Gruppe das 2.3.8.9-Dibenzo-4.7-dimethyl-5.6-dihydro-1.10-phenanthrolin (Cuprotest*) auf einfachem Weg gewinnen.



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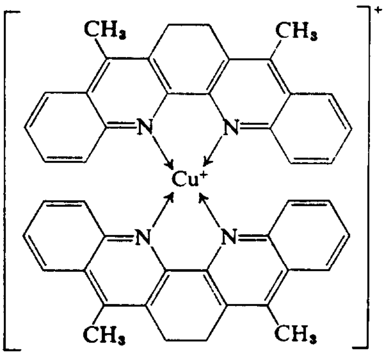
* Hersteller: VEB Laborchemie Apolda.

Wie die genannten Autoren bereits mitteilten, bildet diese Verbindung mit Kupfer(I) einen violetten Bisligandkomplex, der mit organischen Solventien aus der wäßrigen Phase extrahiert werden kann und dem sich folgende Struktur zuordnen läßt:



Obwohl die Autoren auch noch Angaben über das Absorptionsspektrum, den Extinktionskoeffizienten und das Verhalten des Reagenzes gegenüber einigen Metallionen in ihre Veröffentlichung aufgenommen haben, waren für eine umfassende Anwendung noch weitere Untersuchungen erforderlich, über die im folgenden berichtet werden soll.

EXTRAKTIONSVERHALTEN DER KOMPLEXVERBINDUNG

Für die Reduktion des Kupfer(II) erwiesen sich neben Hydroxylammoniumchlorid auch Hydraziniumsulfat, Natriumsulfit und Ascorbinsäure als geeignet. Wie aus unseren Untersuchungen hervorging, ist dabei der Ascorbinsäure der Vorzug zu geben, da hier keine störenden Nebenreaktionen mit Begleitionen zu erwarten sind.

Systematische Versuche zeigten, daß sich im Prinzip die folgenden organischen Lösungsmittel zur Extraktion des in schwach saurer Lösung bei pH 4–5 gebildeten Kupfer(I)–Cuprotest-Komplexes eignen: Butanol, Pentanol, Hexanol, Essigsäureäthyl-, -butyl- und -amylester, Methylisopropylketon, Methylisobutylketon, Chlorbenzol, Methylcyclohexanon sowie Chloroform.

Keine bzw. mit Niederschlagsbildung an der Phasengrenze verbundene geringe Extraktion wurde mit Benzol, Toluol, Diäthyläther, Diisopropyläther, Dichlordiäthyläther, Kohlenstofftetrachlorid, Hexan, Cyclohexan und Heptan beobachtet.

In Abb. 1 ist der Einfluß der Reagenzkonzentration auf den Umfang der Extraktion des Komplexes mit Chloroform dargestellt. Für die Versuche wurde durch Reduktion mit Ascorbinsäure erhaltenes Kupfer(I) bei pH 4–5 in unterschiedlichen Konzentrationsverhältnissen mit Cuprotest umgesetzt, die Extraktion mit dem gleichen Volumen Chloroform durchgeführt und die prozentuale Verteilung radiochemisch mit Hilfe von Kupfer-64 ermittelt. Wird die Probe 15 sec bzw. 5 min nach dem Reagenzzusatz extrahiert, so zeigt sich ein unterschiedlicher Extraktionsverlauf, aus dem die Zeitabhängigkeit der Reaktion hervorgeht. Die gleichen Resultate werden erhalten, wenn das Cuprotest in unterschiedlicher Konzentration vorher im organischen Lösungsmittel gelöst und die wäßrige Phase 15 sec bzw. 5 min geschüttelt wird.

Die Untersuchungen zeigten, daß bereits bei stöchiometrischen Molverhältnissen die Extraktion nahezu quantitativ verläuft, daß jedoch die erforderlich Zeit für

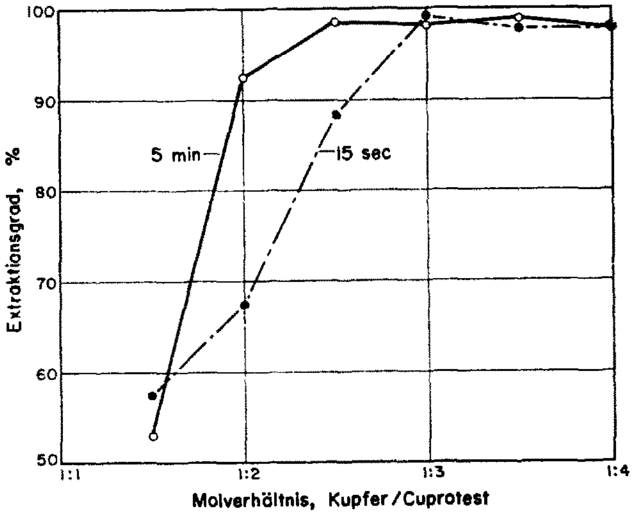


Abb. 1.—Abhängigkeit des Extraktionsgrades des Kupfer(I)-Komplexes von der Reaktionszeit und von der Reagenzkonzentration.

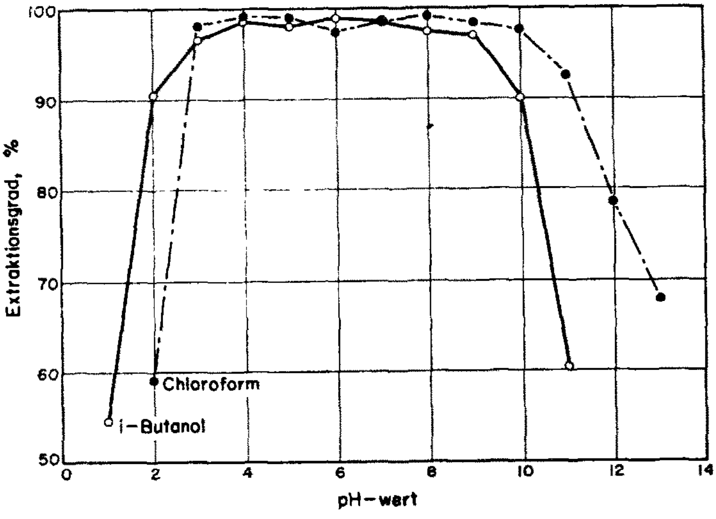


Abb. 2.—Abhängigkeit des Extraktionsgrades des Kupfer(I)-Komplexes für i-Butanol und Chloroform vom pH-Wert.

analytische Zwecke unvorteilhaft lang ist. Durch Erhöhung der Reagenzkonzentration auf das dreifache erfolgt die Reaktion praktisch momentan.

In Abb. 2 ist die pH-Abhängigkeit der Extraktion für i-Butanol und Chloroform wiedergegeben. Die Durchführung erfolgte wie bei der ersten Versuchsreihe unter Variation der pH-Werte, wobei ein fünffacher Reagenzüberschuß angewandt wurde. Vorteilhaft zeigte sich die Verwendung von Chloroform. Das unbrennbare und gegenüber Wasser spezifisch schwerere Lösungsmittel erlaubt bei Mehrfachextraktionen eine einfachere Arbeitsweise. Daß Cuprotest in Chloroform im Gegensatz zu verschiedenen Solventien, wie Methylisobutylketon und Essigsäureäthylester, leicht löslich und die Reagenzlösung wenigstens vier Wochen haltbar ist, spricht ebenfalls für dieses Lösungsmittel. Die bereits von E. Uhlemann und Mitarb.[2] beobachtete Trübung durch Emulsionsbildung kann leicht durch Zentrifugieren beseitigt werden. Bei der Anwendung höherer Alkohole, Ester oder Ketone sind dagegen zusätzliche Trockenmittel erforderlich, wie aus Tabelle I hervorgeht.

TABELLE I.—VERSUCHE ZUR BESEITIGUNG DER EMULSIONSBILDUNG

Lösungsmittel	Extinktionsmittelwert von Doppelproben		
	unbehandelt	zentrifugiert	mit Trockenmittel filtriert
i-Butanol	0,644	0,502	0,375
i-Pentanol	0,511	0,482	0,379
Essigsäure-äthylester	0,623	0,511	0,374
Methyliso-butylketon	0,473	0,460	0,374
Chloroform	0,399	0,379	0,381

Zu den Versuchen wurden 10 μg Kupfer in der wäßrigen Phase bei pH 8 in Gegenwart von 1 ml Weinsäure (10 g/l) mit Ascorbinsäure reduziert und zweimal mit je 5 ml Reagenzlösung (5 mg/100 ml) 15 sec extrahiert. Als Trockenmittel für die auf 10 ml ergänzte organische Lösung wurden jeweils 100 mg wasserfreies Natriumsulfat verwendet. Gemessen wurde in einer 3-cm-Küvette bei 554 nm.

Absorptionsspektrum

In Abb. 3 ist das Absorptionsspektrum des Komplexes in Chloroformlösung dargestellt, das ein Absorptionsmaximum bei 554 nm zeigt, wobei ein molarer dekadischer Extinktionskoeffizient von 7950 l Mol^{-1} cm^{-1} erzielt wird. Diese Werte stimmen etwa mit den Angaben von Uhlemann[2] bei Verwendung von i-Pentanol überein.

Einfluss von Begleitelementen

Literaturangaben zufolge[3] ist die Selektivität der "Cuproin"-Gruppe in sterischen Gegebenheiten begründet. Danach können wegen der Behinderung der Substituenten

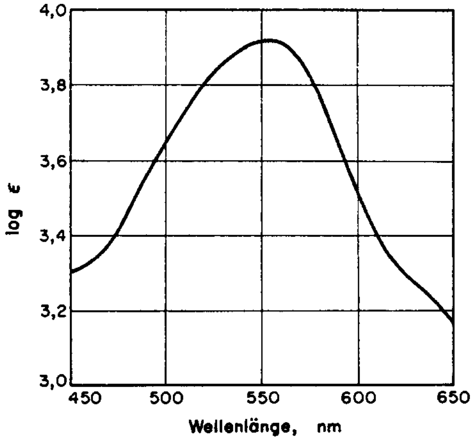


ABB. 3.—Typische Farbkurve der Lösung des Kupfer(I)-Cuprotest-Komplexes in Chloroform.

bei der Chelatbildung mit oktaedrisch konfigurierenden Metallen keine Triligandkomplexe gebildet werden. Besonders günstige Bedingungen sind jedoch bei dem tetraedrisch konfigurierenden Kupfer(I)-Ion gegeben.

Störungen der Reaktion des Kupfer(I) mit Cuprotest sind vor allem durch Bildung schwerlöslicher Hydroxidsalze bzw. Hydroxide, ferner durch Oxydationsmittel und durch komplexbildende Anionen zu erwarten. Unsere Untersuchungen zeigten, daß solche Anionen bereits in geringster Konzentration stören, die wenig dissoziierte oder schwerlosliche Verbindungen mit Kupfer bilden, wie ÄDTA, Thiosulfat, Cyanid und Sulfid. In 1 m Lösungen der Anionen Fluorid, Chlorid, Bromid, Jodid, Thiocyanat, Sulfat, Carbonat, Phosphat, Nitrit, Nitrat, Perchlorat, Borat, Acetat, Tartrat, Citrat und Oxalat konnten keine Störungen der Bestimmung beobachtet werden.

Vorteilhaft erwies sich vor allem, daß die in der analytischen Praxis häufig verwendeten Hilfskomplexbildner wie Tartrat und Citrat die Bestimmung nicht beeinträchtigen, so daß Störungen durch die im interessierenden pH-Bereich als Hydroxide oder Hydroxidsalze ausfallenden Kationen verhindert werden können.

Für folgende Ionen wurde im Konzentrationsbereich 1–10 mg kein Störeinfluß in Gegenwart von Weinsäure sowohl im sauren (pH 4–5) als auch im alkalischen Gebiet (pH 8–9) festgestellt, wobei die Bestimmung in Anwesenheit von 10 μg Cu erfolgte: Aluminium, Antimon(III), Arsen(III), Gold(III), Wismut, Barium, Calcium, Cadmium, Cer(III), Chrom(III), Kobalt(II), Eisen(II), Gallium, Germanium, Quecksilber, Indium, Kalium, Lithium, Magnesium, Mangan(II), Molybdän(VI), Natrium, Niob, Nickel, Palladium, Platin, Blei, Rhenium(VII), Zinn(II), Strontium, Selen, Silber, Tellur, Titan, Thallium(I), Tantal, Vanadin(V), Wolfram(VI), Zirkonium und Zink. In Gegenwart von Silber, Gold, Platin, Quecksilber und Palladium wurde ein durch abgeschiedenes Metall an der Phasengrenze gebildeter geringer Niederschlag beobachtet. Dieser stört aber die Kupferbestimmung im interessierenden Konzentrationsbereich nicht.

ARBEITSVORSCHRIFT UND STATISTISCHE KENNDATEN

Nach der folgenden Arbeitsweise wurde aus 30 Vierfachbestimmungen von Reagenzienblindwerten nach H. Kaiser statistisch eine Nachweisgrenz (3σ-Kriterium) von 0,008 μg/ml ermittelt.

Die Analysenlösung (20–30 ml, 0–50 μg Cu/ml) wird je nach Konzentration der evtl. störenden Begleitelemente mit einer entsprechenden Menge Weinsäurelösung (20 g/100 ml) versetzt. Nach Zugabe von 2 ml Ascorbinsäurelösung (2 g/100 ml) wird mit 2 m Salpetersäure bzw. mit 2 m Ammoniak ein pH-Wert im pH-Bereich zwischen 4 und 10 eingestellt. Ohne Störung der Bestimmung kann auch ein Acetat- oder Ammoniumchlorid-Puffergemisch verwendet werden. Die wäßrige Phase wird in einem Scheidetrichter mit abgemessenen Anteilen Cuprotest–Chloroformlösung (5 mg/100 ml) 15 sec geschüttelt, die vereinigten organischen Phasen werden 1 min bei *ca.* 4000 U/min zentrifugiert und bei 554 nm gegen reines Chloroform photometriert.

Je nach Kupferkonzentration kann das Meßvolumen und die Schichtdicke der Küvette gewählt werden. Dabei bewährte sich folgende Arbeitsweise:

Die Probe wird zunächst zweimal mit je 5 ml Cuprotest-Lösung extrahiert, wobei das farblose Reagenz aus einer Bürette zugegeben wird. Zeigt der zweite Extrakt nur noch eine geringe oder keine Violettfärbung (Kupfergehalte <1 μg/ml), dann kann die Extraktion bereits als praktisch vollständig angesehen werden und die vereinigten organischen Extrakte werden in einer 5-cm-Küvette gemessen.

Zeigt der zweite organische Extrakt noch eine starke Violettfärbung, dann wird mit abgemessenen Anteilen von 5 bzw. 10 ml der Reagenzlösung weiterextrahiert. Das Ende der Extraktion ist erreicht, wenn die organische Phase farblos bleibt. Die vereinigten Extrakte werden zentrifugiet und photometriert.

Wie durch Korrelationsrechnung festgestellt wurde, ist das Lambert-Beersche Gesetz im meßtechnisch noch gut zugänglichen Konzentrationsbereich von 0–50 μg Cu/ml erfüllt. Für eine Doppelbestimmung ist ein Zeitbedarf von *ca.* 10 min erforderlich. Die im Konzentrationsbereich 0,1–5 μg/ml ermittelte relative Standardabweichung* beträgt 1,1 %.

ANWENDUNGSGEBIETE

Bestimmung in Reinststoffen

Für die Bestimmung des Kupfers in Reinststoffen ist es erforderlich, das Matrixelement trotz Gegenwart des Überschusses an Reduktionsmittel im pH-Bereich 4–9 in Lösung zu halten. Diese Bedingungen lassen sich für eine große Zahl von Elementen realisieren, wobei sowohl im sauren als auch im alkalischen Bereich gearbeitet werden kann.

Die Proben werden durch Salzsäure, Salpetersäure, Schwefelsäure oder Königswasser bzw. durch einen Schmelzaufschluß in eine lösliche Verbindung überführt und in Gegenwart von Ascorbinsäure ein geeigneter pH-Wert der Probelösung imp H-Bereich zwischen 4 und 9 eingestellt. Im neutralnahen und im alkalischen Gebiet evtl. auftretende Niederschläge werden durch Weinsäure in Lösung gehalten.

Nach unseren Untersuchungen kann Kupfer in folgenden Elementen und in einer Reihe ihrer Verbindungen nach diesem Verfahren bestimmt werden: Aluminium, Antimon, Blei, Cadmium, Cer, Chrom, Eisen, Gallium, Germanium, Indium, Kobalt, Lanthan, Mangan, Molybdän, Nickel, Niob, Phosphor, Rhenium, Selen, Tantal, Thallium, Thorium, Titan, Vanadin, Wismut, Wolfram, Zink, Zinn, Zirkon sowie in Alkali- und Erdalkalimetallen.

Das Reagenz ist nicht ohne weiteres anwendbar zur Bestimmung von Kupfer in Gold, Platin, Palladium und Silber sowie zur Analyse von Tellur und Selen, da diese Elemente durch Ascorbinsäure ausgefällt werden. Selen kann durch Eindampfen mit konz. Schwefelsäure abgeraucht werden. Chrom(VI) und Thallium(III) müssen vor der pH-Einstellung im sauren Medium reduziert werden, wobei sich neben Ascorbinsäure auch Natriumsulfit bewährte.

Bei Einwaagen von 1 g Probe wurden Nachweisgrenzen bei $8 \cdot 10^{-6}$ % und relative Standardabweichungen im Konzentrationsbereich von $1 \cdot 10^{-4}$ bis $5 \cdot 10^{-3}$ % zwischen 2 und 3 % ermittelt. Der durchschnittliche Zeitbedarf beträgt 15–20 Minuten für eine Doppelbestimmung.

Bestimmung in verschiedenartigen Proben

Die Spezifität des Reagenzes ermöglicht auch Kupferbestimmungen in einer Reihe von Mehrstoffsystemen. So bewährte sich folgende Arbeitsweise zur Untersuchung eines legierten Stahles:

Ein hundert mg Probematerial werden in einem Gemisch aus 5 ml Salzsäure, 1 ml Phosphorsäure und 1 ml Salpetersäure unter Erhitzen aufgelöst und die abgekühlte Probe nach Zugabe von 5 ml Weinsäure (20 g/100 ml) und 2 ml Ascorbinsäure (2 g/100 ml) mit 2m Ammoniak auf pH 8–9 gegen Indikatorpapier eingestellt. Die Probelösung wird in einem Scheidetrichter überführt und das Kupfer wie bereits beschrieben bestimmt.

Der ermittelte Kupfergehalt von 0,229 % zeigte sehr gute Übereinstimmung mit dem im Attest der Probe (Analysentestprobe Nr. 37 des DAMW Magdeburg) angegebenen Gehalt von 0,23 %.

Ähnliche Ergebnisse konnten mit dem Verfahren auch bei der Bestimmung von Kupferspuren in Schlacken, Erzen und organischen Materialien erzielt werden, wobei die für diese Produkte üblichen Aufschlußverfahren der beschriebenen Bestimmungsmethode vorangestellt werden müssen.

Summary—The application of 2,3,8,9-dibenzo-4,7,dimethyl-5,6-dihydro-1,10-phenanthroline (Cuprotest) to the photometric determination of copper is described. The influence of pH and reagent concentration on the extraction has been examined for 20 organic solvents. Copper can be specifically determined in concentrations up to 50 μg/ml by reduction with ascorbic acid and extraction with a chloroform solution of Cuprotest from a tartaric acid solution, pH 3–10, followed by measurement of the absorbance at 554 mμ. The influence of 60 cations and anions has been investigated. Only EDTA, thiosulphate, cyanide and sulphide interfere. The method was used to examine 37 pure materials and various technical and natural products. It has a lower limit of detection of $8 \times 10^{-6}\%$ and a relative standard deviation of 2–3%.

Résumé—On décrit l'application de la 2,3,8,9-dibenzo-4,7-diméthyl 5,6-dihydro-1,10-phénanthroline (Cuprotest) au dosage photométrique du cuivre. On a examiné l'influence du pH et de la concentration du réactif sur l'extraction pour 20 solvants organiques. On peut doser le suivre spécifiquement à des concentrations allant jusqu'à 50 μg/ml par réduction à l'acide ascorbique et extraction avec une solution chloroformique de Cuprotest à partir d'une solution d'acide tartrique, pH 3–10, suivis de la mesure de l'absorption à 554 mμ. On a étudié l'influence de 60 cations et anions. Seuls l'EDTA, le thiosulfate, le cyanure et le sulfure interfèrent. On a utilisé la méthode pour examiner 37 substances pures et divers produits techniques et naturels. La limite inférieure de détection est de $8 \times 10^{-6}\%$ et l'écart type relatif de 2–3%.

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RAPID ULTRA-TRACE DETERMINATION OF BERYLLIUM BY GAS CHROMATOGRAPHY

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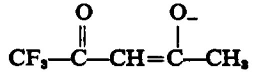
Summary—The electron capture detector has been used to measure ultra-trace quantities of beryllium separated as beryllium(II) trifluoroacetylacetonate by gas chromatographic techniques. The lower limit of detectability is *ca.* 4×10^{-13} g of beryllium. Calibration plots extend from 8×10^{-13} to 4×10^{-11} g of beryllium. Samples of beryllium in aqueous solution at four concentrations ($1{\cdot}18 \times 10^{-7}$, $1{\cdot}18 \times 10^{-8}$, $2{\cdot}95 \times 10^{-9}$, and $8{\cdot}84 \times 10^{-10}$ g/ml) were analysed quantitatively by combining solvent extraction and gas chromatography. The distribution of beryllium during the extraction procedures was determined independently by use of radioactive beryllium-7, but the use of tracers is not required in the recommended procedure. Interference studies were made on cations and anions found in biological samples. At the concentrations used in the extraction procedure and the gas chromatographic process, none of the fifteen ions studied interferes appreciably.

THE analysis of metals by gas chromatography has been the subject of recent intense research activity as a result of the remarkable sensitivity, simplicity, and speed of the technique.[1–18] In addition, interferences by co-occurring elements are much less frequently encountered in the gas chromatographic technique than in other methods for metal analysis, because the components of the sample are simultaneously separated and measured.

The utilization of fluorinated ligands offers significant advantages over the use of the protonated analogues for the formation of volatile metal chelates. The volatility and the excellent response of the electron capture detector for metal complexes derived from trifluoroacetylacetone, the anion of which may be depicted as



$$CF_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH=\overset{\overset{\displaystyle O^-}{|}}{C}-CH_3$$

TFA

make this compound one of the most promising chelating agents in quantitative analyses.[1,8–11] The ease of quantitative extraction with this complexing agent is another attractive quality.[5–7,19,20] Morie and Sweet[5,6] and Moshier and Schwarberg[7] have demonstrated that samples of alloys, and aqueous solutions of mixtures of aluminium, gallium and indium, can be analysed by gas chromatography of metal trifluoroacetylacetonates formed by solvent extraction. In these studies, the sensitivity of the methods developed was limited by the type of detector (thermal conductivity) employed. If electron capture detectors are used, the method becomes much more sensitive. Indeed the technique is more sensitive for some elements than are neutron-activation, atomic-absorption, or other classical methods now in use.

In this study it has been established that beryllium is detectable in quantities as low as 4×10^{-13} g when the electron capture detector is used in the measurement of the trifluoroacetylacetonate chelate. This observation stimulated research to establish a rapid quantitative analytical method for beryllium at extremely low concentrations, based on gas chromatography.

EXPERIMENTAL

Apparatus

Gas chromatography. An ionization detector (diode type) cell, Model A-4150, was used in a Barber Colman Model 20 gas chromatograph. This detector was used in a non-pulsed electron capture mode by reducing the cell potential from a modified power supply. The maximum accessible cell potential was 200 V. The original electrometer was modified to improve the sensitivity. Rearrangement of the circuit provided for stepped multiplication of 1, 2, 5, and 10 times the original signal available to the recorder.

Gas chromatographic columns were fabricated from Teflon (DuPont) tubing because of its inert characteristics. Borosilicate glass was chosen for fabrication of injection port liners. These inert materials served to reduce the likelihood of sample decomposition. As in the chromatography of all potentially toxic compounds, it is strongly recommended that the effluent carrier gas stream be vented to a fume hood, or at least passed through a carefully tended cold trap.

Mixer. The agitation of the reagents during equilibration in the solvent extraction step was achieved by using a Spex Industries, Inc. Mixer/Mill.

Samples (ranging in size from 1 to 10 μl) of the organic solutions were introduced into the glass-lined injection port of the gas chromatography apparatus with a Hamilton microsyringe.

γ-Counter. Model VS1B Well-Type Scintillation Counter and a Model DS1B Scaler purchased from Nuclear Measurements Corporation.

Reagents

Beryllium trifluoroacetylacetonate. The synthesis of beryllium trifluoroacetylacetonate was conducted in a fume hood, with care being exercised to ensure that the samples did not contaminate the laboratory. Metallic beryllium was dissolved in perchloric acid and the solution was used to prepare $Be(TFA)_2$ by solvent extraction.[21] The crystalline product was isolated by evaporation of the benzene layer. The identity and purity of $Be(TFA)_2$ were determined by measuring melting points (authentic samples melt at 112 ± 1° [12,22]) and obtaining emission spectrographic and infrared spectrophotometric data.

We have recently established that powdered samples of elemental beryllium and numerous other metals react directly with trifluoroacetylacetone or other fluorocarbon β-diketones to form the corresponding metal chelates.[13]

Standard solutions were prepared by dissolving weighed amounts of $Be(TFA)_2$ in Mallinkrodt Nanograde-quality or Matheson Coleman and Bell Pesticidequality benzene. The solutions were never stored longer than 24 hr (in polyethylene bottles) before the calibration curve measurements were made. The calibration points were obtained by injecting varying amounts of solutions of three concentrations: $7{\cdot}04 \times 10^{-7}$ g/ml, $1{\cdot}41 \times 10^{-7}$ g/ml, and $2{\cdot}82 \times 10^{-8}$ g/ml (weight of chelate per ml; all other concentrations are expressed in weight of beryllium per ml).

Beryllium. Standard aqueous solutions of beryllium(II) were prepared by dissolving 0·0515 g of high purity metallic beryllium in concentrated perchloric acid, then heating, filtering, and diluting with triply distilled water. Parent solutions were stored in polyethylene bottles, and solutions containing less than 500 ppm were prepared just before the experiments were performed. Four concentrations were used: $1{\cdot}18 \times 10^{-7}$ g/ml, $1{\cdot}18 \times 10^{-8}$ g/ml, $2{\cdot}95 \times 10^{-9}$ g/ml, and $8{\cdot}84 \times 10^{-10}$ g/ml.

Solutions containing tracers were made by adding radioactive ^{7}Be (Nuclear Science and Engineering Corporation) to naturally occurring ^{9}Be solutions. An amount of ^{7}Be sufficient to yield a concentration of 2×10^{-12} g/ml was added after it was determined that this concentration provided a convenient radioactivity level yet did not affect the response of the electron capture detector (1 ml of the radioactive solution produced approximately 80000 counts/min at 950 V).

Trifluoroacetylacetone. For the solvent extraction studies a 0·005M solution of trifluoroacetylacetone (Pierce Chemical Co.) in benzene was employed.

Analytical procedure

A 1·00-ml aliquot of the aqueous solution of beryllium to be analysed was measured into a borosilicate glass culture tube (75 mm × 16 mm, with a volume of 9 ml). To this was added 1·00 ml of a solution of the chelating agent [0·005*M* solution of H(TFA) in benzene] and 1·00 ml of sodium acetate buffer solution (1*M*). The vessel was sealed with a screw cap [fitted with Teflon tape (DuPont) under the cap to prevent leakage]. The tube was then shaken for 1 hr in the Spex Mixer/Mill agitator. The sample was centrifuged until the organic and aqueous layers were completely separated (1 min is adequate). An aliquot of the organic layer (0·50 ml) was transferred to a fresh vial, and an equal volume of 0·01*M* aqueous sodium hydroxide was added to remove the excess of uncomplexed ligand. The mixture was immediately shaken (manually) for 15 sec, the washed organic layer was quickly separated, and the gas chromatographic measurements were made. The washed organic layer was introduced as 1·0-μl (or larger at very low Be concentrations) samples into the gas chromatography apparatus by means of a microsyringe. Five replicate analyses were made. Standard solutions of $Be(TFA)_2$ in benzene were analysed periodically to obtain and check the calibration curve.

Instrument operating conditions

In this investigation the following instrumental operating conditions were utilized.
Column dimensions, 4 ft × 0·06 in. bore, DuPont Teflon
Column packing, 5% SE52 (methyl-phenyl) silicone gum rubber on 60–80 mesh Gas Chrom Z (Applied Science Laboratories)
Column temperature, 80°
Column effluent flow-rate, 50 ml/min
Column inlet pressure, 28 psig
Eluent, prepurified nitrogen
Detector voltage, 10 V
Scavenger flow-rate, 214 ml/min, prepurified nitrogen
Injection port temperature, 168°
Detector temperature, 200°

RESULTS AND DISCUSSION

Beryllium trifluoroacetylacetonate can be quantitatively determined by gas chromatography in even smaller amounts than those reported for other metal trifluoroacetylacetonates. The beryllium chelate is easily eluted and an excellent peak is obtained at a column temperature of 80° (Fig. 1).

A calibration curve was made by analysing standard solutions of $Be(TFA)_2$ in benzene. The calibration curve (Fig. 2) consists of a plot of the chromatographic peak heights and peak areas *vs.* the logarithm of the weight of beryllium. Periodic analyses of freshly prepared standards should be made to ensure that the detector response is stable and unchanged relative to that indicated by previously determined calibration curves. Standard solutions prepared from weighed amounts of $Be(TFA)_2$ can be analysed alternately with the unknowns to recheck the calibration curves.

Solvent extraction methods were used to convert the beryllium in aqueous samples into $Be(TFA)_2$ with concomitant transfer to the organic phase. A substantial excess of the chelating agent must be present to ensure near-quantitative extraction of the beryllium from the aqueous phase and to prevent excessive absorption losses on the walls of the vessels. Trifluoroacetylacetone is eluted just prior to the beryllium chelate and exhibits such pronounced tailing that the presence of large amounts of H(TFA) presented a serious problem because of the overlap of the H(TFA) and $Be(TFA)_2$ chromatographic peaks. This difficulty is illustrated in the first chromatogram in Fig. 1. When the organic phase is washed with sodium hydroxide solution, however, the excess of unreacted ligand is removed from the organic layer, and the interference is eliminated. The second chromatogram in Fig. 1 shows the effect of treatment with the sodium hydroxide solution.

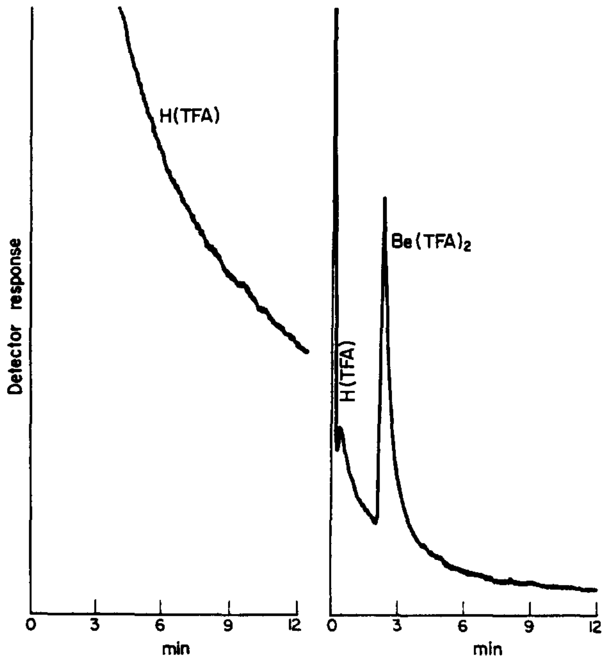


FIG. 1.—Chromatogram obtained from injection of a 1-μl sample of the extracted organic layer before (left) and after (right) washing with aqueous sodium hydroxide. The sample contained $2{\cdot}7 \times 10^{-11}$ g of beryllium.

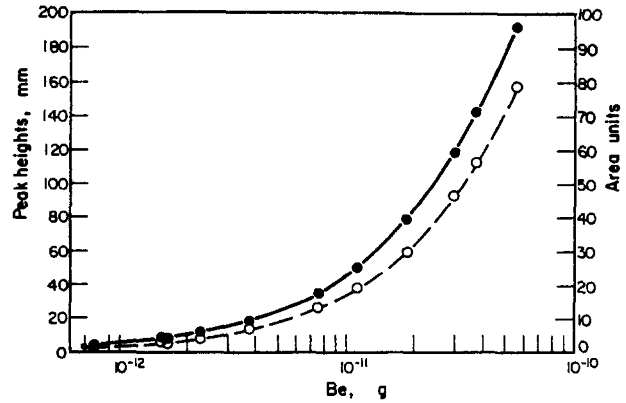


FIG. 2.—Calibration curve prepared from standard solutions of Be(TFA)$_2$ in benzene.
—●— Peak heights; - - -○- - - Peak areas.

Several precautions should be observed in the handling of the extremely dilute samples. At higher concentrations difficulties are not ordinarily encountered, but losses of various ionic and molecular species by adsorption on the walls of storage and reaction vessels becomes much more significant at lower concentrations. One may minimize losses by the use of vessels with low adsorptive properties and by keeping to a minimum the storage time of dilute solutions containing beryllium.

The analytical results obtained on unknowns are shown in Table I. The values obtained are consistently a little low due to losses incurred in the extraction and wash steps. Reasonably good accuracy was achieved considering the extremely small quantities being determined. If greater accuracy is desired, this can be achieved at some loss in convenience and time by the use of tracers to measure the losses and permit recalculation of the beryllium concentration with the losses being taken into account. In four analyses, the losses were determined by independent radiotracer measurements to be 2·5, 2·5, 2·0 and 3·0% respectively. When the losses are taken into account, the relative errors fall to the values shown in the last column of Table II. Accordingly, when tracers are used, the relative errors are reduced from 5·1 to 2·5% for the two $1{\cdot}18 \times 10^{-8}$ g/ml samples, from 6·8 to 4·7% for the $2{\cdot}95 \times 10^{-9}$ g/ml sample, and from 14·9 to 12·1% for the $8{\cdot}84 \times 10^{-10}$ g/ml sample. Experience with particular types of samples in a given concentration range may permit one to estimate loss correction factors that will effectively improve the accuracy without the use of tracers.

TABLE I.—BERYLLIUM DETERMINATION BY GAS CHROMATOGRAPHY WITHOUT TRACERS

Sample no.	Sample size, *μl*	Be detected by G.C., *g*	Be in aqueous phase, *g/ml*	Be measured by G.C., *g/ml*	Mean error, *g/ml*	Relative error, %
1A	0·2	$2{\cdot}12 \times 10^{-11}$	$1{\cdot}18 \times 10^{-7}$	$1{\cdot}06 \times 10^{-7}$	$-1{\cdot}3 \times 10^{-8}$	11·0
1B		$2{\cdot}12 \times 10^{-11}$		$1{\cdot}06 \times 10^{-7}$		
1C		$2{\cdot}14 \times 10^{-11}$		$1{\cdot}07 \times 10^{-7}$		
1D		$1{\cdot}97 \times 10^{-11}$		$0{\cdot}99 \times 10^{-7}$		
Mean		$2{\cdot}09 \times 10^{-11}$		$1{\cdot}05 \times 10^{-7}$		
2A	0·2	$2{\cdot}16 \times 10^{-11}$	$1{\cdot}18 \times 10^{-7}$	$1{\cdot}08 \times 10^{-7}$	$-1{\cdot}1 \times 10^{-8}$	9·3
2B		$2{\cdot}16 \times 10^{-11}$		$1{\cdot}08 \times 10^{-7}$		
2C		$2{\cdot}02 \times 10^{-11}$		$1{\cdot}01 \times 10^{-7}$		
2D		$2{\cdot}18 \times 10^{-11}$		$1{\cdot}09 \times 10^{-7}$		
Mean		$2{\cdot}13 \times 10^{-11}$		$1{\cdot}07 \times 10^{-7}$		
3A	1·0	$1{\cdot}14 \times 10^{-11}$	$1{\cdot}18 \times 10^{-8}$	$1{\cdot}14 \times 10^{-8}$	$-6{\cdot}0 \times 10^{-10}$	5·1
3B		$1{\cdot}13 \times 10^{-11}$		$1{\cdot}13 \times 10^{-8}$		
3C		$1{\cdot}15 \times 10^{-11}$		$1{\cdot}15 \times 10^{-8}$		
3D		$1{\cdot}10 \times 10^{-11}$		$1{\cdot}10 \times 10^{-8}$		
3E		$1{\cdot}10 \times 10^{-11}$		$1{\cdot}10 \times 10^{-8}$		
Mean		$1{\cdot}12 \times 10^{-11}$		$1{\cdot}12 \times 10^{-8}$		
4A	1·0	$1{\cdot}14 \times 10^{-11}$	$1{\cdot}18 \times 10^{-8}$	$1{\cdot}14 \times 10^{-8}$	$-6{\cdot}0 \times 10^{-10}$	5·1
4B		$1{\cdot}13 \times 10^{-11}$		$1{\cdot}13 \times 10^{-8}$		
4C		$1{\cdot}16 \times 10^{-11}$		$1{\cdot}16 \times 10^{-8}$		
4D		$1{\cdot}08 \times 10^{-11}$		$1{\cdot}08 \times 10^{-8}$		
4E		$1{\cdot}10 \times 10^{-11}$		$1{\cdot}10 \times 10^{-8}$		
Mean		$1{\cdot}12 \times 10^{-11}$		$1{\cdot}12 \times 10^{-8}$		
5A	1·0	$2{\cdot}88 \times 10^{-12}$	$2{\cdot}95 \times 10^{-9}$	$2{\cdot}88 \times 10^{-9}$	$-2{\cdot}0 \times 10^{-10}$	6·8
5B		$2{\cdot}69 \times 10^{-12}$		$2{\cdot}69 \times 10^{-9}$		
5C		$2{\cdot}79 \times 10^{-12}$		$2{\cdot}79 \times 10^{-9}$		
5D		$2{\cdot}63 \times 10^{-12}$		$2{\cdot}63 \times 10^{-9}$		
5E		$2{\cdot}74 \times 10^{-12}$		$2{\cdot}74 \times 10^{-9}$		
Mean		$2{\cdot}75 \times 10^{-12}$		$2{\cdot}75 \times 10^{-9}$		
6A	8·0	$6{\cdot}11 \times 10^{-12}$	$8{\cdot}84 \times 10^{-10}$	$7{\cdot}64 \times 10^{-10}$	$-1{\cdot}32 \times 10^{-10}$	14·9
6B		$5{\cdot}84 \times 10^{-12}$		$7{\cdot}30 \times 10^{-10}$		
6C		$5{\cdot}84 \times 10^{-12}$		$7{\cdot}30 \times 10^{-10}$		
6D		$6{\cdot}15 \times 10^{-12}$		$7{\cdot}69 \times 10^{-10}$		
6E		$6{\cdot}15 \times 10^{-12}$		$7{\cdot}69 \times 10^{-10}$		
Mean		$6{\cdot}02 \times 10^{-12}$		$7{\cdot}52 \times 10^{-10}$		

TABLE II.—IMPROVEMENT OF ACCURACY BY SIMULTANEOUS USE OF TRACERS WITH GAS CHROMATOGRAPHY MEASUREMENTS

Sample no.	Be taken in aqueous phase, *g/ml*	Be measured by G.C., *g/ml* (av. of 5 runs)	% Be lost, determined by tracer measurements	Corrected result based on tracer measurements, *g/ml*	Relative error %, with tracer corrections
3	$1{\cdot}18 \times 10^{-8}$	$1{\cdot}12 \times 10^{-8}$	2·5	$1{\cdot}15 \times 10^{-8}$	2·5
4	$1{\cdot}18 \times 10^{-8}$	$1{\cdot}12 \times 10^{-8}$	2·5	$1{\cdot}15 \times 10^{-8}$	2·5
5	$2{\cdot}95 \times 10^{-9}$	$2{\cdot}75 \times 10^{-9}$	2·0	$2{\cdot}81 \times 10^{-9}$	4·7
6	$8{\cdot}84 \times 10^{-10}$	$7{\cdot}52 \times 10^{-10}$	3·0	$7{\cdot}77 \times 10^{-10}$	12·1

It is expected that this analytical technique should be useful in biomedical systems for determination of trace amounts of beryllium. Previous workers[23–27] have discussed in detail the digestion and dissolution of a variety of samples to prepare aqueous solutions for analysis. It was necessary to design experiments to determine whether several naturally occurring cations and anions interfere in either the extraction or the chromatographic steps of the analysis. Table III shows the results of the interference studies. None of the species evaluated caused any appreciable interference at the concentrations used. Scribner[19] noted that strong interference occurred in the extraction of beryllium when fluoride was present at a concentration of 0·25*M*. He has recently independently confirmed that fluoride concentrations below $10^{-4}M$ do not interfere with the extraction of beryllium.[21] At intermediate fluoride concentrations partial extraction occurs. Consequently, if fluoride concentrations greater than $10^{-4}M$ are expected, tracers should be used to establish the percentage of beryllium extracted.

TABLE III.—INTERFERENCE STUDIES ON THE EXTRACTION AND G.C. ANALYSIS OF BERYLLIUM(II)

Compound	Concentration, *g/ml*	Be, *g/ml*	Ratio	$Be(TFA)_2$ peak heights, *mm*	
				With anion or cation	Without anion or cation
A. Anions					
$CaCl_2{\cdot}2H_2O$	$9{\cdot}70 \times 10^{-6}$	$5{\cdot}37 \times 10^{-8}$	200/1	120	120
$Ca(H_2PO_4)_2{\cdot}H_2O$	$1{\cdot}99 \times 10^{-6}$	$5{\cdot}37 \times 10^{-8}$	40/1	120	120
KNO_3	$9{\cdot}94 \times 10^{-6}$	$5{\cdot}37 \times 10^{-8}$	200/1	120	120
Na_2SO_4	$2{\cdot}41 \times 10^{-5}$	$5{\cdot}37 \times 10^{-8}$	400/1	120	120
NaF	$6{\cdot}01 \times 10^{-6}$	$5{\cdot}37 \times 10^{-8}$	100/1	121	120
Mixture of anions					
$CaCl_2{\cdot}2H_2O$	$5{\cdot}82 \times 10^{-6}$	$5{\cdot}37 \times 10^{-8}$	564/1	119	120
$Ca(H_2PO_4)_2{\cdot}H_2O$	$1{\cdot}19 \times 10^{-6}$				
KNO_3	$5{\cdot}96 \times 10^{-6}$				
Na_2SO_4	$1{\cdot}45 \times 10^{-5}$				
NaF	$6{\cdot}01 \times 10^{-6}$				
B. Mixture of cations					
Al	$1{\cdot}40 \times 10^{-6}$	$1{\cdot}18 \times 10^{-8}$	118/1	10	10
Co	$1{\cdot}40 \times 10^{-6}$				
Cu	$1{\cdot}40 \times 10^{-6}$				
Fe	$1{\cdot}40 \times 10^{-6}$				
Mg	$1{\cdot}40 \times 10^{-6}$				
Mn	$1{\cdot}40 \times 10^{-6}$				
Zn	$1{\cdot}40 \times 10^{-6}$				

It is significant that quantitative extractions can be effected in the presence of EDTA.[19] Therefore, should it be necessary, gross quantities of numerous co-occurring metal ions could be retained in the aqueous layer by use of this masking agent.

If desired, the effective sensitivity of this technique could probably be improved by various modifications. Since only a very small portion (5 μl) of the organic phase is used in the chromatographic analyses, perhaps the organic solution could be concentrated to improve the effective sensitivity. An alternative approach is to use smaller aliquots of benzene with higher concentrations of the chelating agent, thereby producing a greater concentration of the complex in the benzene layer after extraction. These options could be exercised in addition to the obvious expedient of preconcentration of the aqueous solution to be analysed.

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Zusammenfassung—Mit dem Elektroneneinfangdetektor wurden Ultraspurenmengen Beryllium gemessen, die gaschromatographisch als Beryllium(II)-trifluoracetylacetonat abgetrennt wurden. Die untere Nachweisgrenze ist etwa $4 \cdot 10^{-13}$ g Beryllium. Eichkurven gehen von $8 \cdot 10^{-13}$ bis $4 \cdot 10^{-11}$ g Beryllium. Berylliumproben in wäßriger Lösung wurden bei vier Konzentrationen ($1{,}18 \cdot 10^{-7}$, $1{,}18 \cdot 10^{-8}$, $2{,}95 \cdot 10^{-9}$ und $8{,}84 \cdot 10^{-10}$ g/ml) quantitativ durch Kombination von flüssig-flüssig-Extraktion und Gaschromatographie analysiert. Die Verteilung von Beryllium während der Extraktionsvorgänge wurde unabhängig mit radioaktivem Beryllium bestimmt, der Gebrauch von Tracern ist jedoch bei dem empfohlenen Verfahren nicht notwendig. Die Störung durch in biologischen Proben vorkommende Kat- und Anionen wurde untersucht. Bei den bei der Extraktion und bei der Gaschromatographie verwendeten Konzentrationen stört keines der untersuchten fünfzehn Ionen merklich.

Résumé—On a utilisé le détecteur à capture d'électrons pour mesurer des ultra-traces de béryllium séparé à l'état de trifluoroacétylacétonate de béryllium(II) par des techniques de chromatographie en phase vapeur. La limite inférieure de détection est d'environ 4×10^{-13} g de béryllium. Les courbes d'étalonnage vont de 8×10^{-13} à 4×10^{-11} g de béryllium. On a analysé quantitativement des échantillons de béryllium en solution aqueuse à quatre concentrations ($1{,}18 \times 10^{-7}$, $1{,}18 \times 10^{-8}$, $2{,}95 \times 10^{-9}$ et $8{,}84 \times 10^{-10}$ g/ml) en combinant l'extraction par solvant et la chromatographie en phase vapeur. Le partage du béryllium pendant les techniques d'extraction a été déterminé indépendamment par l'emploi de béryllium radioactif mais l'utilisation de traceurs n'est pas nécessitée par la technique recommandée. On a étudié l'interference de cations et d'anions que l'on trouve dans des échantillons biologiques. Aux concentrations utilisées dans la technique d'extraction et la méthode de chromatographie en phase vapeur, aucun des quinze ions étudiés ne gêne de façon appréciable.

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FLAVONES AS ANALYTICAL REAGENTS—A REVIEW

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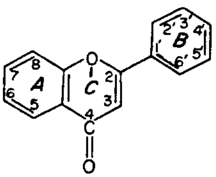
Summary—A review is given of the use of flavones as spectrophotometric, fluorimetric and gravimetric reagents for metals and a few non-metals.

FLAVONES are compounds of plant origin, the study of which has given insight into such subjects as fermentation of tea, tanning of leather, manufacture of cocoa and flavour of foodstuffs. Flavonoids are used as anti-oxidants, flavonols being better than other flavones. The α,β-unsaturated ketonic structure of the pyrone ring, a free hydroxyl group in the 3-position and the free *o*-dihydroxy grouping are responsible for the anti-oxidant activity.[1] Geissman's recent book[2] presents an excellent review of almost all aspects of flavonoid chemistry except the analytical utility of the compounds. In the present communication, the usefulness of these compounds as analytical reagents is reviewed. They are sensitive and can be made selective by controlling the pH, extracting the complex into some suitable solvent or by using appropriate masking agents.

The flavonoid nucleus is composed of two units, the C_6 unit ring A, and the C_6–C_3 fragment, rings B and C, numbered as shown in (I):



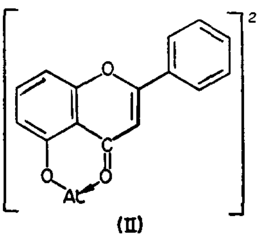
(I)

The reactions of rings *A* and *B* are more or less those of any aromatic compound but the reactions of the pyrone ring *C* are typical of the flavones. Although ring *C* contains the carbonyl group a flavone does not react with carbonyl reagents such as hydroxylamine, semicarbazide or phenylhydrazine. Treatment with alkali opens the pyrone ring to yield a 1:3 diketone which may be further degraded. The carbonyl group together with the double bond constitutes a conjugated system which accepts hydrogen in different modes.

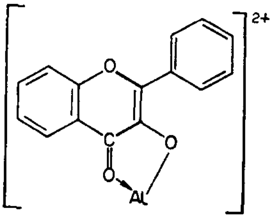
Flavonoids contain a highly conjugated aromatic system and consequently exhibit intense and characteristic absorption spectra, usually measured in ethanol. Dissociation of the flavonoid or chelation with various reagents[3–12] causes shifts in the spectra which give additional information regarding the structure of the flavonoid. Flavones and flavonols (3-hydroxyflavones) generally exhibit two regions of intense absorption which fall in the ranges 320–380 mμ (Band I) and 240–270 mμ (Band II).[13]

Complex-formation by flavonoids with aluminium has long been used for the detection of certain hydroxy groups in these compounds. Flavonoids which do not contain a free hydroxyl group at position 3 or 5 are unable to form complexes on addition of aluminium chloride solution and their spectra are not significantly changed by addition of this reagent.

5-Hydroxyflavones form stable yellow complexes of type (II).[14] The complexation leads to appreciable bathochromic shifts of Bands I and II.



(II)



(III)

Flavonols form complexes with aluminium which are stable even in dilute hydrochloric acid. The complexation of the 3-hydroxyl group with the metal results in a flavylium structure (III) which is greatly stabilized by its partly aromatic character.[14]

Chelation can also take place when two hydroxy groups are present *ortho* to each other in ring *B*.[14] By virtue of these chelating centres the flavonoids react with metal ions, sometimes quite selectively, and owe to this their analytical importance. Considerable use has been made of the flavonoids in the detection and determination of ions. On the other hand, the study of the metal complexes has revealed a number of more or less specific tests for the presence of certain hydroxy groups in the flavone molecule. For example, Kanno[15] has shown that niobium is chelated by flavonoids in acid solution by means of a carbonyl group and a hydroxyl group *ortho* to each other. In neutral solution niobium also reacts by means of two *o*-hydroxy groups in ring *B*. 5-Hydroxyflavones do not form complexes with niobium. Similarly, it has been concluded[16–18] that the formation of an orange chelate with the uranyl ion is a positive test for the presence of the 5-hydroxy group in the flavone molecule.

The flavonoids which have been most used as analytical reagents are flavonols such as morin, quercetin, galangin, robinetin, myricetin, *etc*. They are more sensitive than the 5-hydroxyflavones, which are also used as reagents. The compounds can either be extracted from the specific plant or synthesized. The preparations of the analytically important compounds are briefly indicated.

Morin (3,5,7,2′,4′-*pentahydroxyflavone*). It occurs in the wood of *Artocarpus integrifolia*[19] and *Toxylon pomiferum*[20] and can be synthesized.[21,22] The ground heartwood of *Artocarpus integrifolia*[23] is extracted for 6 hr with ten times its weight of boiling water, and the light brown extract, while still hot, is treated with lead acetate solution till precipitation is complete. The lead salt is filtered off and decomposed with hydrogen sulphide. Morin, thus obtained, is crystallized from acetic acid as colourless needles (m.p. 300°, d.). The compound is also commercially available.

Quercetin (3,5,7,3′,4′-*pentahydroxyflavone*). To extract[24] this commercially available compound, the flower petals of red or yellow roses are extracted with boiling ethanol and the alcoholic solution concentrated under reduced pressure. The impurities are removed by repeatedly shaking the concentrate with petroleum ether. After the residue has been boiled with 7% sulphuric acid for 2 hr, it is extracted with ether to yield a mixture of quercetin and kaempferol. The quercetin is stripped from the ether extract with aqueous borax solution and then precipitated by addition of acid (m.p. 312°). It can also be synthesized.[25]

Galangin (3,5,7-*trihydroxyflavone*). It is extracted from the sodium carbonate soluble portion of the ether extract of the rhizomes of *Alpinia officinarum Hance*[26] and the wood of *Pinus griffithii*.[27] Robinson and co-workers[28,29] have synthesized the flavonol (m.p. 217–218°).

Robinetin (*3,7,3′,4′,5′-pentahydroxyflavone*). This commercially available compound occurs in the wood *Robinia pseudoacacia*[30] and is synthesized[31] by heating *in vacuo* a mixture of ω-methoxyresacetophenone, and the sodium salt and anhydride of trimethylgallic acid; robinetin 3,3′,4′,5′-tetramethyl ether is obtained. Demethylation of the ether with hydriodic acid gives robinetin.

Myricetin (*3,5,7,3′,4′,5′-hexahydroxyflavone*). The compound (m.p. 357–360°) is isolated from the leaves,[32] wood,[33] berries, bark and stem[34,35] of many plants, or can be synthesized.[36]

Quercetagetin (*3,5,6,7,3′,4′-hexahydroxyflavone*). It can be extracted from the flowers of *Tagetes erecta*[37] and the wood of *Acacia catechu*.[38] Its synthesis is given by Baker *et al.*[39] and it melts at 325°.

METAL COMPLEXES

Flavonoids form complexes with metal ions such as Al(III), Be(II), Fe(III), Mo(VI), U(VI), Th(IV) and Zr(IV). Many of the complexes fluoresce and many are an intense yellow or orange. The structures in most cases are only tentatively suggested.

Aluminium

An alcoholic solution of morin[40–42] reacts with aluminium ions in neutral or acetic acid medium to give an intensely green fluorescent compound with structure of type(II). It also reacts with Be,[43] Ga, In, Th and Sc[44,45] but the reactions are pH-dependent. On dropping neutral or slightly acidic test solution (containing not less than 0·005 μg of Al) on filter paper impregnated with morin, a green fluorescence appears which can be observed in ultraviolet light and is resistant to $2M$ hydrochloric acid. Zirconium interferes. The fluorescence reaction has also been used in determination of aluminium.[46,47] Schantl[42] reported a 1:3 complex, but a 1:1 complex has also been reported.[47] Quercetin[48] has also been used for determination of aluminium.

Beryllium

In alkaline solution beryllium[49,50] produces a yellowish green water-soluble fluorescent compound[51] with morin, which in contrast to the aluminium complex is stable towards alkali. The reaction can be made specific for beryllium by masking interfering ions such as Ti(IV), Sn(IV), Al, Fe(III), Cr(III), Mg and Ca with ammoniacal EDTA.[52] Sandell[53] has developed the reaction into a very sensitive fluorimetric method (sensitivity 0·001 ppm) for beryllium. The estimation is done in strongly alkaline medium with potassium cyanide and EDTA as masking agents, and the fluorescence is excited with 365-mμ radiation. The method has been further improved[54] to detect submicrogram quantities (0·0004 μg of Be) and to determine 0·2 μg of beryllium with a precision of about 1%.

Boron

The use of morin has been described for the fluorimetric[55] and spectrophotometric[56] determination of boron. A solution containing boron is made alkaline with sodium carbonate, evaporated nearly to dryness and neutralized with $1M$ hydrochloric acid. This is followed by addition of 1·5 ml each of $1M$ hydrochloric acid, 0·1% oxalic acid solution and 0·02% alcoholic morin solution and the mixture is evaporated to dryness on a water-bath and then heated in an air-oven at 110° for 30 min. The residue is extracted with acetone and made up to 25 ml in the same solvent. After 30 min the fluorescence of the acetone extract relative to 10^{-4}% sodium fluoresceinate (uranine) solution is measured. Beer's law is obeyed over the range 0·5–12 μg of boron.

Quercetin, by virtue of its similarity to morin in reactive grouping, is also used in the photometric determination of boron.[57] The coloured borate–quercetin complex has a mole ratio of 1:1 and obeys Beer's law over the range 0–0·50 ppm of boron at 445 mμ. The method has been applied satisfactorily to determine boron in graphite samples.

Gallium

A method for determination of gallium is based on the chloroform extraction of a fluorescent compound from *ca.* 1*M* hydrochloric acid solution treated with cupferron and morin.[58] The method, however, lacks selectivity.

Germanium

Germanium[59,60] forms a yellow complex with quercetin between pH 6·4 and 7·1. The complex has maximum absorption at 410 mμ. The reagent has been suggested for determination of germanium but it is not selective.

Hafnium

Quercetin has been used for spectrophotometric determination of hafnium in zirconium.[61] The method is based on the effect of hydrogen peroxide on the zirconium–quercetin complex. It is claimed that 0·1 mole % of hafnium in zirconium can be estimated.

Iron

The reaction of iron(III) with quercetin to give an olive green colour is used to detect iron with a sensitivity of 3 μg of iron.[62] The compound quercitrin behaves in a similar way.

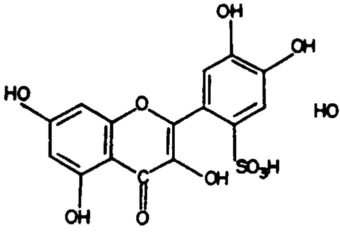
Molybdenum

Flavonols are amongst the most sensitive reagents used for spectrophotometric estimation of molybdenum, but lack selectivity, so a prior separation of molybdenum is essential. The complexes formed by interaction of molybdate with various flavonoids such as morin,[63,64] quercetin,[65] dihydroquercetin,[66] galangin[67] and robinetin[68] have been studied. The yellow morin complex[64] is extracted with isobutyl methyl ketone in hydrochloric acid medium to avoid interference due to certain foreign ions. In this method, Be, Mg, Al, Ti(IV), Zr, Th, As(III) and Cr(III) can be tolerated in amounts up to 10 times that of the molybdenum present. The ratio of molybdenum to morin in the complex is 1:1 and the formation constant is $1{\cdot}2 \times 10^5$. Goldstein *et al.*[65] have developed a method in which molybdenum is extracted into a solution of α-benzoinoxime in chloroform, after which the complex of molybdenum and quercetin is formed in a portion of the organic extract by the addition of quercetin in ethanol. The absorbance of the yellow complex is measured at 420 mμ. The method has been used in determination of molybdenum in thorium oxide, uranyl nitrate, and steel. The complex contains molybdenum and quercetin in the ratio 1:1 and its instability constant is $1{\cdot}1 \times 10^{-5}$. Dihydroquercetin[66] has also been used for determining molybdenum in steel. The 1:1 molybdenum–galangin complex[67] has maximum absorption at 405 mμ, constant between pH 2·0 and 3·2. The complex obeys Beer's law from 2 to 30 μg of molybdenum per 12 ml and its stability constant is $3{\cdot}8 \times 10^4$

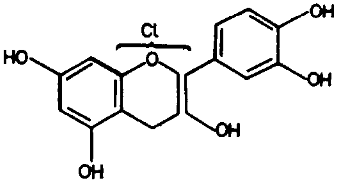
at pH 2·7. The sensitivity of the reaction is 0·0063 μg Mo/cm^2 for an absorbance of 0·001. Robinetin[68] forms two complexes with molybdenum, the molar ratios being 1:1 and 2:1 (Mo:Rob). Between pH 2·0 and 3·5 the absorbance is constant. The sensitivity of the reaction is 0·002 μg of molybdenum and it obeys Beer's law from 0·08 to 0·56 ppm of molybdenum. The dominant species in the molybdenum–myricetin[69] system contains the two constituents in equimolar ratio. The absorbance is maximal and constant between pH 1·5 and 2·5 and its stability constant has been found to be $4{\cdot}2 \times 10^4$ (at pH 2·0).

Niobium

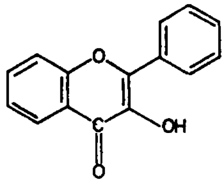
Quercetinsulphonic acid [QSA—(IV)] reacts with niobium[70] either in neutral or in acid solution to give yellow complexes. In neutral solution λ_{max} shifts to longer wavelengths with increase in pH. The absorbance remains constant in the pH range 5·8–6·5. In sulphuric acid medium maximum absorption is at 412 mμ for an acidity $< 0{\cdot}45N$ and 428 mμ for acidity $> 1{\cdot}8N$. The system obeys Beer's law and the molar absorptivity is $14{\cdot}8 \times 10^3$. In an attempt[15] to locate the functional group in the reaction between quercetinsulphonic acid and niobium, the reactions of some of the flavonoids such as cyanidin chloride (V), flavonol (VI) and naringenin (VII) were investigated.



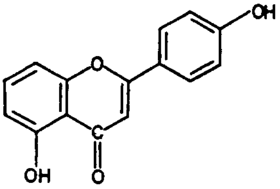
(IV)



(V)



(VI)



(VII)

They react with niobium in acid medium by means of a carbonyl and a hydroxy group *ortho* to each other, but in neutral medium by means of either two *o*-hydroxy groups or a carbonyl and a hydroxy group *ortho* to each other. The complexes formed at pH 3·5 and 6·0 are 1:2 (Nb:QSA) and those formed in $7{\cdot}2N$ and $0{\cdot}23N$ sulphuric acid, having absorption maxima at about 428 and 412 mμ respectively, are 1:1.

Niobium has been precipitated from homogeneous solution with 3, 5, 7, 3′, 4′-pentahydroxyflavonone (dihydroxyquercetin) as reagent.[71] In boiling acid medium and the presence of air the flavone is transformed into 3, 5, 7, 3′, 4′-pentahydroxyflavone (quercetin) which precipitates the niobium chelate. Zirconium and molybdenum do not interfere but titanium must be absent or present only in traces. If tantalum is present, it is precipitated first, with a small amount of niobium, from sulphuric acid solution containing ammonium oxalate; niobium remains in solution and is then precipitated at higher acidity. The small amount of niobium oxide in the tantalum oxide can be quickly and reliably determined spectrophotometrically with concentrated sulphuric acid and hydrogen peroxide.

Phosphorus

An indirect fluorimetric method[72] has been developed for determining trace quantities of phosphate. The method depends on the ability of the phosphate to quench the aluminium–morin fluorescence. Ions that compete with aluminium for morin or are highly coloured interfere, and phosphate must be separated from them. Of the chelates of aluminium, gallium and zirconium with morin, 3-hydroxyflavone and quercetin, the aluminium–morin system has been found to be the most satisfactory for determination of phosphate.

Rare earths

The complexation between flavonoids and rare earths has been investigated.[73,74] The studies include the reactions of morin, quercetin, kaempferol (3,5,7,4′-tetrahydroxyflavone), diosmetin (5,7,3′-trihydroxy-4′-methoxyflavone), apigenin (5,7,4′-trihydroxyflavone), fisetin (3,7,3′,4′-tetrahydroxyflavone), naringenin, myricetin, robinin (3,7-diglucoside of kaempferol) and rutin (3-glucoside of quercetin) with praseodymium, gadolinium, holmium and yttrium as representatives of different families of rare earths. The reagents which do not contain a 3-hydroxy group or which have this group blocked are incapable of forming complexes with lanthanides. The complexes are formed through the 3-hydroxy and 4-carbonyl groups and contain lanthanide and flavonoid in the ratio 1:1 or 1:2. Holmium complexes are more stable, possibly owing to the lanthanide contraction.

Scandium

Morin has been suggested as a sensitive fluorescence reagent for scandium[54] in neutral or slightly acidic medium. Scandium salts of organic acids can be extracted from aqueous medium into organic solvents such as butyl alcohol, ethyl acetate and amyl alcohol. Morin is mixed with the organic phase to produce a greenish fluorescence.

Tantalum

Tantalum has been precipitated in the same way as niobium from homogeneous solution with dihydroxyquercetin[71] as reagent. The small amount of niobium which co-precipitates can be estimated spectrophotometrically with concentrated sulphuric acid and hydrogen peroxide. Zirconium and molybdenum do not interfere but titanium must be absent.

Thorium

The flavonoids rank among the extremely sensitive reagents for determination of thorium. Quercetin[75] forms a yellow complex with thorium and exhibits λ_{max} from 420 to 425 mμ. The absorbance of the complex is constant from pH 2·7 to 3·5 and it obeys Beer's law over a concentration range of 10 to 150 μg of thorium in 25 ml. The complex contains quercetin and thorium in the ratio 2:1 and its dissociation constant is approximately $1{\cdot}2 \times 10^{-10}$. Many ions interfere seriously but thorium can be effectively separated by a combination of ion-exchange separation and thenoyltrifluoroacetone extraction. In the presence of ascorbic acid and thiocyanate, 5–10 times as much iron, uranium and rare earths do not interfere with the thorium estimation.[76]

The reaction between thorium and morin takes place in slightly acid chloride or nitrate solution to give the 1:2 (Th:Mor) complex.

The reaction is instantaneous and quite sensitive (0·007 μg ThO_2/cm^2 for an absorbance of 0·001 at 410 mμ). It has been used for spectrophotometric[77] and fluorimetric[78] determination of thorium. In a method[79] for estimating thorium in urine, with morin as reagent, inorganic constituents are removed by double precipitation with hydrofluoric acid in the presence of lanthanum as collector.

Complex formation between thorium and rutin[79] (molar ration 1:2) has been used for absorptiometric determination of thorium. The complex obeys Beer's law over the concentration range 1·16–23·2 ppm of thorium and its absorption spectrum is constant between pH 3·0 and 4·0. Kanno[81] has reported the formation of two yellow coloured chelates at different pH values with quercetinsulphonic acid. The compound is used for determination of thorium. Other flavonoids investigated include robinetin,[68] myricetin,[69] galangin,[82] melanoxetin,[83] chrysin,[84] 3-methylgalangin[85] and norwogonin.[86] The flavonols are 4–5 times more sensitive towards thorium than the 5-hydroxyflavones are. The complexes are 1:1. The stability constants range from 10^4 to 10^5.

Tin

Morin gives an intense light green fluorescence in contact with traces of ammoniacal tin solution[49] (sensitivity 0·05 μg of Sn). The reagent also gives fluorescence with other alkaline metal solutions, but the reaction with tin can be made specific by using a solution containing SnS_3^{2-} ions, obtained by treating the tin solution with yellow ammonium sulphide and subsequently adding dilute hydrogen peroxide. Flavonol[87] has been used for the fluorimetric determination of tin(IV) in 0·5–1*N* sulphuric acid medium.

Titanium

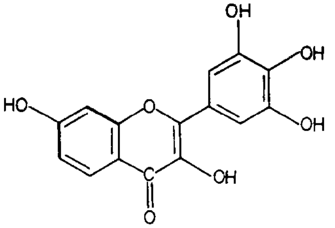
Acidic titanium[88] solution reacts with morin to give a yellowish brown chelate in which titanium is bound in an anionic species. The interferences due to zirconium and thorium is eliminated by precipitating them with phosphoric acid. Iron(III) should be reduced to iron(II). The test is quite sensitive and the limit of identification of titanium is 0·01 μg. Titanium has been determined with morin by dispersing the insoluble complex in polyvinyl alcohol to obtain a clear solution; in this way, 1–50 μg of titanium can be determined spectrophotometrically at 420 mμ, the λ_{max} of the complex.[89]

Titanium(IV) reacts with rutin[90] (3-glucoside of quercetin) giving a deep orange-red water-soluble complex (λ_{max} 440 mμ). The complex is very stable and obeys Beer's law in the concentration range 0·09–1·92 ppm of titanium. The intensity of colour does not vary between pH 5·2 and 7·5. Surprisingly, large amounts of interfering ions such as fluoride, oxalate, phosphate, citrate and borate can be tolerated. A preliminary investigation showed that titanium and galangin[91] form a 1:2 complex.

Uranium

Many polyhydroxy flavonoids have been used as analytical reagents for spectrophotometric determination of uranium, both the 3-hydroxy and 5-hydroxyflavones having been found useful for the purpose. The flavonols without a 5-hydroxy group give a yellow colour with uranyl ions, and the 5-hydroxyflavones give an orange colour. Compounds containing both the 3- and 5-hydroxy groups give an orange colour, showing that chelation involves the 5-hydroxy and the carbonyl groups. Morin,[92–94] quercetin,[95] quercetinsulphonic acid,[96] flavonol,[97], galangin[98] and its 3-methyl derivative,[85] 5-hydroxyflavone[99] and its 7-methoxy[99] and 7,8-dimethoxy derivatives,[100] norwogonin,[86] rutin[101] and robinetin[102] have been used for determinaton of uranium. Flavonol forms with uranyl ion a yellow complex which is sparingly soluble in common organic solvents. Spectrophotometric determination has been carried out by extracting the complex with tri-n-butyl phosphate.

All the complexes formed contain metal and ligand in the ratio of 1:1 or 1:2. In the case of robinetin, however, two complexes containing metal and the ligand in the molecular ratios 1:1 and 2:1 are obtained. There are two chelating centres in the robinetin molecule (VIII), the 3-hydroxy and the carbonyl group, and a pair of *o*-hydroxy groups in ring *B*. Both centres can chelate separate uranyl ions simultaneously and hence the formation of 1:1 and 2:1 complexes is explained, assuming that the remaining uranyl co-ordination sites, if any, are occupied by water molecules or anions. The compounds are all extremely sensitive but not selective. A prior separation of interfering ions is essential.



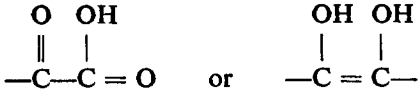
(VIII)

Vanadium

The product obtained on treating vanadium with quercetin[103] is a green water-soluble chelate which is adsorbed on the reagent precipitated by dilution (sensitivity 0·25 μg of V). The reaction has been used in a spot-test for vanadium. Rutin[104] has been used for the same purpose, and for determination of vanadium.[105] The orange complex formed is water-soluble, has λ_{max} at 435 mμ, obeys Beer's law in the concentration range 0·51–14·3 ppm of vanadium, and does not vary in colour intensity between pH 3·5 and 6·0. The composition of the complex is 1:2 (V:rutin) and the logarithm of its stability constant is 9·82.

Zirconium

Amongst the reagents used for determination of micro amounts of zirconium, those preferred contain the group



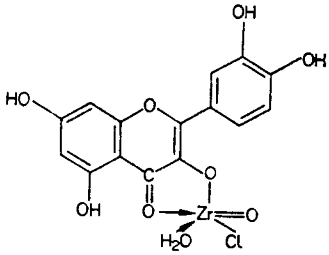
$$\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}\overset{\overset{\text{OH}}{|}}{\text{C}}=\text{O} \quad \text{or} \quad \text{—}\overset{\overset{\text{OH}}{|}}{\text{C}}=\overset{\overset{\text{OH}}{|}}{\text{C}}\text{—}$$

and thereby form a stable five-membered ring, with zirconium replacing one or two hydrogen atoms. Other metal ions can form similar complexes, but most of these, in contrast to zirconium complexes, are extensively dissociated in mineral acid medium. Consequently, hydroxyflavones have been used as sensitive reagents for zirconium. Flavonols form 1:1 or 2:1 (Flav:Zr) complexes and 5-hydroxyflavones form 1:1 complexes. Zirconium tends to form complexes mainly with the flavonols, these complexes being 100 times more stable[106,107] than the 5-hydroxyflavone complexes.

A method based on the blue fluorescence given by zirconium and flavonol in 0·2*N* sulphuric acid medium has been developed for the fluorimetric determination of zirconium.[108] The method is especially useful for minerals containing less then 0·25% of ZrO_2. The degree of dissociation of the 1:1 complex has been calculated[109] from the relationship between the absorption spectrum and the excitation spectrum of the zirconium–flavonol chelate. Spectrophotometric determination of zirconium with flavonol has also been used.[107]

Zirconium forms an intensely fluorescent complex with morin in strongly acidic solution (optimum acidity 1*M* hydrochloric acid).[110] The predominant fluorescing species formed has a 1:2 molar ratio of zirconium to morin and it appears that the 1:1 complex is also formed. The fluorescence intensity conforms to Beer's law up to 1·5 ppm or even higher concentrations. Zirconium can be determined in the presence of many other cations which give fluorescence, if a small amount of EDTA is added and the change in intensity is measured. The zirconium fluorescence is destroyed, but the fluorescence due to the other ions remains unchanged because these metals are not appreciably complexed by EDTA at the high acidity used. Morin has also been used as an absorptiometric reagent,[111] its yellow zirconium complex having λ_{max} at 436 mμ. The method has been used to determinate zirconium in magnesium alloys.[112]

An acidic zirconium solution treated with quercetin[113] produces an intense yellow colour suitable for the determination of 0·1–50 μg of ZrO_2. The procedure involves the separation of zirconium from interfering elements by precipitation with *p*-dimethylaminoazophenylarsonic acid before its estimation with quercetin. The optimum acidity is 0·5*M* hydrochloric acid. Two complexes are formed, 1:1 and 2:1 having ratios of quercetin to zirconium, with equilibrium constants $K_1 = 3{\cdot}3 \times 10^{-5}$ and $K_2 = 1{\cdot}3 \times 10^{-9}$. On the basis of chemical analysis the 1:1 complex has been formulated as (IX):



(IX)

Micro quantities of zirconium in presence of milligram quantities of interfering elements (particularly iron, vanadium and titanium) have been determined fluorimetrically with quercetin.[114] The method involves extraction of zirconium with 2-thenoyltrifluoroacetone and development of fluorescence with the reagent. The precision of the method is ±4·0%.

Galangin,[115] melanoxetin,[115] robinetin[116] and quercetagetin[117] have been put forward as analytical reagents for spectrophotometric determination of zirconium. They are extremely sensitive and selectivity is achieved by using a highly acidic medium in which the complexes formed by interfering ions are dissociated.

Zusammenfassung—Es wird eine Übersicht über die Verwendung von Flavohen als spektrophotometrische, fluorimetrische und gravimetrische Reagentien für Metalle und einige Nichtmetalle gegeben.

Résumé—On présente une revue sur l'emploi des flavones comme réactifs spectrophotométriques, fluorimétriques et gravimétriques pour les métaux et quelques composés non métalliques.

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ANALYTICAL APPLICATIONS OF TERNARY COMPLEXES—V[*]

INDIRECT SPECTROPHOTOMETRIC DETERMINATION OF CYANIDE

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Summary—An indirect spectrophotometric method is proposed for the determination of cyanide down to 0·2 ppm. It is based on the fact that cyanide prevents the formation of the strongly absorbing ternary complex between silver(I), 1,10-phenanthroline and Bromopyrogallol Red in nearly neutral aqueous solution. Among 17 cations examined, only mercury(II) could not be tolerated. Zinc, cadmium and cobalt interfered only when present in large amounts. A 1000-fold molar excess (over cyanide) of 14 anions can also be tolerated. Bromide, iodide and thiocyanate interference is overcome by addition of lead nitrate, ammonium sulphate and barium nitrate, followed by centrifugation.

THE need for very sensitive methods for measuring cyanide is obvious and new colour reactions involving cyanide are especially worthy of examination in the absence of a satisfactory standard method. There are at present two main colorimetric methods, both based on the König reaction and proposed by Aldridge[1,2] and Epstein.[3] However, both are subject to many disadvantages. For example, in Aldridge's method or its modifications use is made of amines having dangerous physiological properties, *e.g.*, benzidine and β-phenylenediamine,[4,5] and Epstein's method involves a relatively unstable reagent, pyrazolone. Bark and Higson's method[4] uses an isosbestic point and thus requires the use of a spectrophotometer rather than a filter instrument.

In the proposed procedure use is made of the inhibiting effect of cyanide ions on the formation of the blue colour in neutral aqueous solution of the silver/1,10-phenanthroline/Bromopyrogallol Red complex.[6] This sensitive ternary reaction ($\varepsilon_{635m\mu} = 5{\cdot}1 \times 10^4$) can be made virtually specific for silver among cations by the use of EDTA and, in some instances, fluoride and hydrogen peroxide.

EXPERIMENTAL

Reagents

The following solutions were prepared as described in Part IV[7] and the apparatus was the same.

Potassium cyanide, $10^{-5}M$.
Silver nitrate, $10^{-5}M$.
1,10-*Phenanthroline*, $10^{-3}M$.
Bromopyrogallol Red, $10^{-4}M$. (BPR)
Ammonium acetate, 20%.
EDTA, *ca*. 0·1*M*, (3% w/v).

Procedure

By pipette transfer 1–10 ml of cyanide solution (approximately $10^{-5}M$) into a 50-ml volumetric flask, and add 10 ml of $10^{-5}M$ silver nitrate, 1 ml of 3% EDTA solution, 1 ml of 20% ammonium acetate solution to give a pH between 6 and 8, 1 ml of $10^{-3}M$ 1,10-phenanthroline and 4 ml of $10^{-4}M$ BPR. Dilute the solution to 50 ml with distilled water, mix, and within 30 min measure the absorbance at 635 mμ in a 1-cm cuvette against a blank solution containing no cyanide or silver.

A plot of absorbance *vs*. concentration of cyanide is linear over the range 0·26–2·6 ppm of cyanide. Use $10^{-5}M$ potassium cyanide, 1–10 ml, for preparation of a calibration curve.

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[*] Part IV—*Talanta*, 1966, 13, 1667.

RESULTS AND DISCUSSION

Optimization of conditions

Wavelength of measurement. A solution containing BPR and 1,10-phenanthroline at *ca.* pH 7 exhibits maximum absorbance at 570 mμ. The addition of silver ions decreases this peak and builds up another at 635 mμ. The addition of cyanide ions reverses this action. Because an excess of dyestuff (BPR) is used to develop the ternary system, it is better to measure a decrease in the complex peak at 635 mμ rather than an increase in the free reagent peak at 570 mμ.

pH. The blue complex can be developed, and inhibited by cyanide ion, over the pH range 3–10. However, because of the susceptibility of BPR to oxidation in alkaline solution, and the obvious difficulties associated with using cyanide ion in acidic solution, a suitable pH for colour development was considered to be 6–8.

TABLE I.—INTERFERENCE STUDIES

Cations	Molar excess over cyanide	Absorbance at 635 mμ
Ag	—	0·120
Al	100	0·121
Au	100 (10)	0·007 (0·119)
Ba	100	0·120
Bi	100	0·120
Ca	100	0·119
Cd	100 (10)	0·145 (0·116)
Co(II)	100 (1)	0·157 (0·120)
Cu(II)	100	0·127
Fe(III)	100	0·125
Hg(II)	100 (1)	0·245 (0·235)
K	100	0·120
Li	100	0·118
Mg	100	0·122
Mn(II)	100	0·125
Na	100	0·120
Ni	100	0·130
Pb	100	0·120
Pd	100 (10)	0·190 (0·122)
Zn	100 (50)	0·137 (0·117)

Reagent excesses. For the development of the ternary complex at least a 4-fold and 10-fold molar excess of BPR and 1,10-phenanthroline respectively over silver must be present.[6] In view of the sensitivity of the reaction ($\varepsilon_{635\text{m}\mu} = 5{\cdot}1 \times 10^4$), a working range of 0·26–2·6 ppm of cyanide can be achieved by using 10 ml of 10^{-5} M silver nitrate, 4 ml of $10^{-4}M$ BPR and 1 ml of $10^{-3}M$ 1,10-phenanthroline solution in a final volume of 50 ml. The reaction is instantaneous and the absorbance is constant for 30 min. In addition, it is possible to tolerate up to a 10000-fold molar excess of EDTA over the most concentrated cyanide solution used.

More concentrated solutions of cyanide can be examined by suitably increasing the concentrations of the reagents. This aspect was not pursued further.

Interferences. The effect of a 100-fold molar excess over cyanide of 19 cations in the presence of a 500-fold molar excess of EDTA over cyanide was examined and the results are shown in Table I. Where an interference was encountered a lower cation level was examined and these are shown in brackets. The order of addition was cyanide (5·2 μg), cation, silver, EDTA, 1,10-phenanthroline, buffer and BPR. The absorbances were read against a solution containing no cyanide or silver ions.

It may be concluded that only cadmium, cobalt(II), gold(III), mercury(II), palladium(II) and zinc showed any significant interference. It was found that cadmium, gold and palladium could be tolerated at a 10-fold level, cobalt(II) at an equimolar level and zinc at a 50-fold level. Only mercury(II) continued to interfere at an equimolar level. This is obviously because of the high stability constant of the mercury(II)–cyanide complex in comparison with the silver–cyanide and mercury(II)–EDTA complexes. In this case all of the silver ions are free to form the blue ternary complex.

The following 14 anions were examined in a manner similar to the cations: acetate, bromide, carbonate, chloride, chromate, fluoride, iodide, nitrate, perchlorate, persulphate, phosphate, sulphate, sulphite and thiocyanate. A 1000-fold molar excess over cyanide of acetate, fluoride and nitrate, and a 100-fold molar excess of carbonate, chloride, perchlorate and sulphate did not interfere. The interference of a 1000-fold molar excess of sulphate can be prevented by adding excess of barium nitrate and centrifuging to remove the precipitate. A 1000-fold molar excess of barium does not interfere. Chromate, persulphate, phosphate and sulphite up to a 1000-fold molar excess over cyanide can be treated in the same way. The interference of bromide, iodide and thiocyanate is not affected by this modification of the procedure, and direct masking of these and other anions is not possible because any cation capable of forming a stable complex with them would interfere with the determination, if present in excess. A satisfactory procedure for overcoming the interference is to precipitate the lead salts of these anions and then to remove the excess of lead by precipitation with ammonium sulphate and then the excess of sulphate with barium nitrate. All the precipitates are centrifuged together, and the free cyanide is determined in the separated aqueous phase. It is possible to mask the excess of lead ions with EDTA after removal of the lead precipitate (which would dissolve in EDTA if not removed) but it was considered wise to make use of any "collector" properties offered by the lead and barium sulphates to remove traces of bromide, iodide and thiocyanate. The addition of barium nitrate ensures that a large excess of ammonium sulphate can be added if necessary. This procedure, although somewhat involved, was found to be effective in determining traces of cyanide in the presence of 1000-fold molar excesses of bromide, iodide and thiocyanate.

Precision. The relative standard deviation obtained from multiple analyses of a series of ten solutions, each containing 5·2 μg of cyanide, was found to be 3·4%.

Zusammenfassung—Zur Bestimmung von Cyanid bis herunter zu 0,2 ppm wird eine indirekte spektrophotometrische Methode vorgeschlagen. Sie beruht auf der Tatsche, daß Cyanid die Bildung des stark absorbierenden ternären Komplexes aus Silver(I), 1,10-Phenanthrolin und Brompyrogallolrot in etwa neutraler wäßriger Lösung verhindert. Unter 17 untersuchten Kationen durfte nur Quecksilber(II) nicht anwesend sein. Zink, Cadmium und Kobalt störten nur in großen Mengen. Ein 1000-facher molarer Überschuß (über Cyanid) von 14 Anionen ist ebenfalls tragbar. Die Störung von Bromid, Jodid und Rhodanid beseitigt man durch Zugabe von Bleinitrat, Ammoniumsulfat und Barium-nitrat mit nachfolgendem Zentrifugieren.

Résumé—On propose une méthode spectrophotométrique indirecte pour le dosage du cyanure en quantités aussi petites que 0,2 p.p.m. Elle est basée sur le fait que le cyanure empêche la formation du complexe ternaire fortement absorbant entre l'argent (I), la 1,10-phénanthroline et le rouge de bromopyrogallol en solution aqueuse sensiblement neutre. Parmi 17 cations examinés, seul le mercure(II) ne peut être toléré. Le zinc, le cadmium et le cobalt ne gênent que s'ils sont présents en fortes quantités. On peut aussi tolérer un excès 1000 fois molaire (par rapport au cyanure) de 14 anions. Les interférences du bromure, de l'iodure et du thiocyanate sont évitées par l'addition de nitrate de plomb, de sulfate d'ammonium et de nitrate de baryum, suivie d'une centrifugation.

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DETERMINATION OF PALLADIUM, PLATINUM AND RHODIUM IN GEOLOGIC MATERIALS BY FIRE ASSAY AND EMISSION SPECTROGRAPHY*

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Summary—A method is described for the determination of palladium down to 4 ppb (parts per billion, 10^9), platinum down to 10 ppb and rhodium down to 5 ppb in 15 g of sample. Fire-assay techniques are used to preconcentrate the platinum metals into a gold bead, then the bead is dissolved in *aqua regia* and diluted to volume with $1M$ hydrochloric acid. The solution is analysed by optical emission spectrography of the residue from 200 μl of it evaporated on a pair of flat-top graphite electrodes. This method requires much less sample handling than most published methods for these elements. Data are presented for G-1, W-1, and six new standard rocks of the U.S. Geological Survey. The values for palladium in W-1 are in reasonable agreement with previously published data.

PROCEDURES for the determination of palladium, platinum and rhodium are available in the literature, but many are only suitable for much higher concentrations than that of most geologic materials which the U.S. Geological Survey is called upon to analyse. Some procedures require considerable time and analytical skill and are generally cumbersome and not too reliable in routine use. Still other procedures are designed for one of the three elements, giving little attention to the other two. The method described here is relatively free from extensive sample manipulations, adequately sensitive, and can determine all three elements in essentially a single procedure.

EXPERIMENTAL

Fire assay

Gold (weighing between 0·80 and 1·20 mg), which is used as a collector for the platinum metals, is added in the form of 0·007 in. dia. wire to yield approximately the same concentration of gold in the final solution as in the spectrographic standards. A piece of lead foil ½ in. square and 0·016 in. thick is sharply folded at the center with pliers. The fold is then opened, the gold wire placed in the centre of the crease, the fold closed on the wire and again folded at the centre to give a thickness of four layers. All edges are then crimped with pliers to ensure enclosure of the wire. This lead envelope is added as the last step in the preparation of the fusion mixture described below.

The fusion and cupellation steps in general follow conventional fire-assay practices as described by Bugbee[1] and are only summarized here to point out variations found helpful. A flux is formed by combining sodium carbonate, lead(II) oxide, silica, borax glass and calcium fluoride together with flour as a reducing agent or potassium nitrate as an oxidizing agent. These are combined in a "30-g" fireclay crucible with a maximum capacity of about 260 ml. The amounts of the flux components are dependent on the composition of the sample to be analysed. The object is to form at least a two-phase melt: a liquid slag approximating to a complex borosilicate, and a metallic lead phase, controlled in size, to collect the noble metals present. The addition to the flux of 1–3 g of calcium fluoride, not

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routinely used in gold fire-assaying, has been found beneficial for many types of samples analysed for the platinum metals.

After the flux components are in the crucible, 15 g (or 30 g) of sample are added and the contents thoroughly mixed. Then the lead foil containing the gold wire is added. Part of the borax glass for the charge may be added as a cover for a 30-g sample, or for a sample liable to form dust, or for a sample relatively rich in iron(III) oxide.

The crucible is placed in the muffle of an assay furnace preheated to a temperature of 850–900°. After the door is closed the temperature is raised to 1050–1120° over a period of 30–45 min. The crucible is then removed and the molten charge is poured into an iron mould and allowed to cool. The slag is carefully chipped and worked away from the lead with a hammer and brush, and the lead is tapped into a cube, producing the lead button.

The lead of the lead button is separated from its noble metal content by cupellation. The cupels, made of compressed bone ash, are placed in the furnace, preheated to 950–1000°, for about 10 min. Then the lead buttons are placed in the cupels and the furnace door closed until the lead melts and a bright surface is formed on the lead. The door is opened and the temperature first lowered to about 830°, then gradually raised to a finishing temperature of about 900° as the lead is oxidized and the oxide absorbed by the cupel. The cupellation is finished when only a noble metal bead remains on the cupel. Since silver is not to be determined, higher temperatures may be used than in the conventional silver assay, thus reducing the dangers of "freezing" (lead oxide covering the molten lead and preventing further oxidation).

Once the bead is obtained, the cupel is removed from the furnace and allowed to cool. No precautions are necessary to prevent "sprouting" as in the silver assay, since there is about 1 mg of gold present. The bead is examined under a stereoscopic microscope (about 45 × magnification) while still on the cupel and the colour, surface, and shape are noted. The presence of certain elements is indicated when the colour has drastically changed from that of gold. No correlation, as yet, has been made with the shape or surface of the bead and the presence or concentration of specific elements. This is still under investigation.

The bead is then carefully transferred and weighed. Relatively pure gold beads are nearly spherical and need more care in handling than hemispherical silver beads. No attempt is made to clean the bead, *e.g.*, by brushing, thus avoiding any losses of metals. The small amount of lead-saturated bone ash retained on the bead adds little to the weight and is easily dissolved in the subsequent treatment. The weight of the gold wire added to the flux initially is compared with the weight of the bead obtained. Any sizable gain (or slight loss) is noted and aids in calculating the dilution factor if the weight has substantially increased.

The bead is transferred to a 1-ml volumetric flask to which 0·1 ml of *aqua regia* (3:1 hydrochloric acid:nitric acid) is added, and allowed to stand overnight at room temperature. To ensure complete dissolution of the bead, the solution is heated for 15–20 min on a steam-bath. After the bead has dissolved, an aliquot of a 4 mg/l solution of molybdenum (the internal standard) in $2M$ hydrochloric acid is added so that the concentration is 0·2 mg of molybdenum per l. after dilution to volume with $1M$ hydrochloric acid. All beads analysed to date have been soluble in *aqua regia*. However, if any metals remain undissolved, the presence of other platinum metals should be suspected.

When a sample is known from a previous semi-quantitative spectrographic analysis to be high in platinum metals, the amount of gold is increased so that a 2:1 ratio of gold to total platinum metals is obtained. This ratio has been found satisfactory for dissolution of the platinum alloys. Larger volumetric equipment and more acid may then be necessary as stated by Murt and Corson.[2] Dilutions are made from the solution to obtain a desirable concentration for measurement of the platinum metals. Gold in solution (10 mg/ml) is added to the final dilution in order that the gold concentration be about 1000 mg/l and approximately equivalent to the concentration of gold in the standards.

Spectrographic analysis

Two ¼-in. dia. flat-top, graphite electrodes are first waterproofed with 4 drops each of a petroleum ether solution of Apiezon "N" grease (5 g/l). Then 100 μl of the unknown sample or the standard, both containing the internal standard, are added to each electrode in 50-μl increments and evaporated by means of a heat lamp. The electrodes are kept under the heat lamp until placed in the arc-spark stand. Each exposure consists of exciting the residue of 200 μl of solution on the two electrodes[3]. The sample-bearing electrodes are then placed in the arc-spark stand and the residue is excited and the spectrum recorded, with the apparatus and operating conditions listed in Table I.

The emulsion is calibrated by means of an iron bead arced at 5 A d.c. and exposed for 15 sec at a transmission of 4·8%. The formation of the iron bead is described by Haffty.[4] The iron lines and relative intensities used for plate calibration were selected from a list of homologous lines.[5,6] They are reproduced in Table II for the convenience of the reader. The calibration curve is established by plotting transmission (ordinate) *vs.* intensity (abscissa) on log–log paper.

TABLE I.—APPARATUS AND SPECTROGRAPHIC OPERATING CONDITIONS

Excitation source—intermittent d.c. arc. Primary power source—full-wave rectified 280-V, 60-cycle power supply—initiated by a high-voltage condensed spark synchronized to initiate each half cycle.	
Radio-frequency current,	2·0 A
Initiating circuit parameters	
Capacitance,	0·0025 μF
Inductance,	15 μH (residual)
Primary resistance,	16 Ω (dial setting 5)
Secondary resistance,	0·5 Ω (residual)
Discharge voltage,	15,000 V
Number of discharges per half cycle,	11
Current, radio-frequency,	7·0 A
Spectrograph—folded, 3-m Rowland circle-mounted grating with 21,000 lines/in. giving a reciprocal linear dispersion of 4 Å/mm in the first order.	
Wavelength region,	2400–3600 Å
Slitwidth,	40 μ
Illumination,	arc image focused on grating
Analytical gap,	3 mm
Transmission,	100%
Exposure,	20 sec
Emulsion,	Kodak SA-1
Electrodes,	ASTM type C-3

TABLE II.—IRON LINES USED FOR PLATE CALIBRATION

Fe line, Å	Intensity	Fe line, Å	Intensity
3157·89	73	3217·38	165
3175·45	125	3222·07	625
3178·02	94	3225·99	770
3196·93	470	3239·44	285
3205·40	210	3251·24	62
3215·94	225	3268·24	29

TABLE III.—ANALYTICAL LINES USED IN DETERMINATION OF PALLADIUM, PLATINUM AND RHODIUM

Element	Analytical line, Å	Concentration range based on analytical curve, *mg/l*
Pd	Pd 3242·70	0·05–5·0
	Pd 3404·58	0·025–0·5
Pt	Pt 2659·45	0·125–5·0
	Rh 2490·77	0·125–5·0
Rh	Rh 3396·85	0·05–5·0
	Rh 3434·89	0·05–1·25

The Mo 2816·15 Å line was used as internal standard line throughout.

Each plate contains the exposures of 10 or 11 samples in duplicate, plus 9 standards and one iron bead to calibrate the emulsion. After the plate has been processed, transmittance measurements of selected analytical and internal standard lines (Table III) are obtained by means of a microphotometer. From the calibration curve, intensity values are obtained for the standards which are used in constructing the analytical curves. The analytical curves are established by plotting the ratio of the intensities of the analytical and internal standard lines *vs.* concentration on logarithmic coordinates. The concentrations of the elements in the unknown samples are read from the analytical curves. The absolute weight of metal is calculated from the volume of solution in which the bead was dissolved. This weight is then divided by the weight of sample taken to give ppm or ppb [parts per billion (10^9)] in the sample.

Preparation of standards

Stock solutions, calculated to contain 1000 mg of the element per l., are made by dissolving the ammonium salts of the appropriate chloro-complexes in 2*M* hydrochloric acid. These stock solutions are then serially diluted with 2*M* hydrochloric acid to give concentrations of 100, 50, 25, 10, . . . 0·5 mg/l.

The standards for analysis are made by transferring 0·2 ml of a gold stock solution (10 mg/ml) to each of nine 2-ml volumetric flasks. To these, 0·1 ml each of the palladium, platinum and rhodium solutions are added. In addition to this, 0·1 ml of a solution of molybdenum (4 mg/l) in 2*M* hydrochloric acid is added as the internal standard and the mixtures are diluted to volume with 1*M* hydrochloric acid. The resulting standards contain palladium, platinum and rhodium in concentrations of 50, 5, 2·5, 1·25, 0·5 . . . 0·025 mg/l in solutions containing gold (1000 mg/l) and molybdenum (0·2 mg/l).

RESULTS

The precision of the method is illustrated by the results in Table IV. The standard deviations were obtained by running several 15-g portions of the same sample on various plates at different dates.[2,7]

Table IV.—Data on precision of method

Element	Average concentration, *ppm*	S.D.	C.V.	*n*
Palladium	0·426	0·023	5·4	5
Platinum	0·395	0·0077	1·9	5
Rhodium	0·0143	0·0008	5·6	2

d = difference between duplicate values.
n = number of duplicate determinations.
$\bar{X}$ = average of the individual results.
S.D. = $\sqrt{(\Sigma d^2/2n)}$ = standard deviation.
C.V. = $100(\text{S.D.})/\bar{X}$ = coefficient of variation.

In order to obtain an indication of the accuracy of the method at concentrations present in geological materials, aliquots of known solutions of palladium, platinum and rhodium were added to 15-g portions of quartz sand, evaporated under heat lamps, and carried through the method described. The solutions were added in 0·1-ml increments and distributed over the surface of the sand, which had previously been heated for about 20 min in an evaporating dish. The total amount of solution added to any one dish was no more than 0·6 ml and with proper care the solution did not seep through the sand to the evaporating dish. After the sand was added to the fire clay crucible, the additional precaution was taken of dry-rinsing the evaporating dish with the soda needed for the charge and then transferring this to the crucible. However, the platinum in samples 10 and 11 was accurately weighed and added as the metal. The results are presented in Table V.

For low-grade platinum ores, 30 g (approx 1 assay ton) have been used. When the weights of the elements given in Table V are considered on the basis of this weight of sample, they represent a concentration range of 17 ppb to 4·23 ppm.

The analytical results for G-1, W-1, and six new standard rocks are presented in Table VI. Each run is the average of duplicate determinations. More detailed data on the localities from which the six new standard rocks were collected, and the results for many elements, were presented by Flanagan.[8]

TABLE V.—RECOVERY OF PALLADIUM, PLATINUM AND RHODIUM ADDED TO QUARTZ SAND

Sample No.	Palladium			Platinum			Rhodium		
	Added	Recovered		Added	Recovered		Added	Recovered	
	μg	μg	%	μg	μg	%	μg	μg	%
1	0·50	0·54	108	0·50	0·55	110			
2	1·0	1·15	115	1·0	1·12	112			
3	0·50	0·57	114	2·0	2·02	101	0·50	0·57	114
4	1·0	1·13	113	5·0	4·40	88	1·0	1·01	101
5	5·0	4·9	98	5·0	4·95	99			
6	5·0	4·78	96	10	9·65	96	5·0	5·4	108
7	20	20·8	104	20	20·9	104			
8				100	106	106			
9	100	93	93	100	102	102			
10	100	94	94	113	103	91			
11				127	126	99			

DISCUSSION

Fire assay

To obtain maximum recovery of the platinum metals from a sample, it is a great help to know its approximate mineral or chemical composition so that the proper combination and proportions of the constituents of the assay flux can be selected. The tabular material below shows flux compositions used for a granite and a peridotite; all quantities are in grams.

	Granite (G-1)		Peridotite (PCC-1)
Ore	15	30	15
Na_2CO_3	20	30	35
PbO	50	60	32
SiO_2	1	0	6
Borax glass	3	3	35
CaF_2	1	1	1
Flour (for 28-g lead button)	3	3	5 (excess to reduce all PbO)

Relatively high concentrations of certain minerals or elements may require special treatment. Beamish[9] stresses the problem of analysing for platinum metals in the presence of large amounts of nickel. Large amounts of organic matter such as coals require careful oxidation to avoid losses. Placer concentrates create separate problems, and slags from certain finely ground chromite ores may show considerable amounts of unattacked chromite when examined under a microscope. Hence, fire assaying for platinum metals is more involved than routine fire assaying for gold.

Results

The results for palladium in W-1 shown in Table VI are in reasonable agreement with previously published data.[10] The platinum content in W-1, although varying slightly for different weights of sample taken (15 and 30 g), is ascribed a weighted average of 18 ppb. Two different lots of the dunite (DTS-1) were used for the two runs and this may account for the apparent slight variation in the platinum content.

TABLE VI.—PALLADIUM, PLATINUM, AND RHODIUM CONTENT IN STANDARD ROCKS

U.S.G.S. sample no.	Rock type	Weight of sample, *g*	Pd, *ppb*		Pt, *ppb*		Rh, *ppb*	
			1	2	1	2	1	2
G-1	Granite	30	<4		<10		<5	
W-1	Diabase	30	14		16		<5	
W-1		15	14		22		<5	
G-2	Granite	30	<4		<10		<5	
GSP-1	Granodiorite	30	<4		<10		<5	
AGV-1	Andesite	30	<4		<10		<5	
BCR-1	Basalt	30	<4		<10		<5	
BCR-1		15	<4		<10		<5	
PCC-1	Peridotite	15	7	7	15	15	<5	<5
DTS-1	Dunite	15	<4	<4	11	<10	<5	<5

The elements listed in the table have been assigned conservative "limits of determination." It will be noted that these limits are the same for both 15- and 30-g samples. Lower limits for the 30-g samples are possible and in favourable instances have been obtained. However, until more data are available the conservative figure given seems advisable.

The term "limit of determination" is used here to mean that if the element in question were present in the sample in a concentration at or above this limit, not only would its presence be detected, but also its concentration could be stated, each with a reasonable degree of certainty. Below this limit the element, in a given sample, may be detected (and under favourable conditions may be stated) but, even with equal care, there is a reasonable chance it may be missed.

Zusammenfassung—Ein Verfahren zur Bestimmung von Palladium bis herunter zu 4 ppb (Teile pro Milliarde 10^9), Platin bis 10 ppb und Rhodium bis 5 ppb in 15 g Probe wird beschrieben. Durch Schmelzverfahren werden die Platinmetalle in einer Goldperle vorangereichert; dann wird die Perle in Königswasser gelöst und mit 1 M Salzsäure zur Marke aufgefüllt. Die Lösung wird analysiert durch optische Emissionsspeltrographie des Rückstandes, der beim Verdampfen von 200 μl auf ein Paar flachen Graphitelektroden zurückbleibt. Diese Methode erfordert viel weniger Arbeitsgänge mit der Probe als die meisten bekannten Vorschriften für diese Elemente. Ergebnisse für G-1, W-1 und sechs neue Standardgesteine des US Geological Survey werden mitgeteilt. Die Palladiumwerte in W-1 stimmen befriedigend mit früher publizierten Daten überein.

Résumé—On décrit une méthode pour le dosage du palladium jusqu'à des quantités aussi petites que 4 p.p.b. (parties par billion, 10^9), du platine jusqu'à 10 p.p.b. et du rhodium jusqu'à 5 p.p.b. dans 15 g d'échantillon. On utilise des techniques de grillage pour préconcentrer les métaux du platine dans une perle d'or, puis la perle est dissoute dans l'eau régale et diluée au volume à l'acide chlorhydrique $1M$. On analyse la solution par spectrographie d'émission optique du résidu obtenu en en évaporant 200 μl sur une paire d'électrodes de graphite à tête plate. Cette méthode nécessite beaucoup moins de manipulation d'échantillon que la majeure partie des méthodes publiées pour ces éléments. On présente les données pour G-1, W-1 et six nouvelles roches étalons du U.S. Geological Survey. Les valeurs pour le palladium dans W-1 sont en accord raisonnable avec les données antérieurement publiées.

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CATION-EXCHANGE BEHAVIOUR OF SEVERAL ELEMENTS IN HYDROFLUORIC ACID–ORGANIC SOLVENT MEDIA

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Summary—The cation-exchange characteristics of 15 elements with the strongly acidic cation-exchange resin Dowex 50 × 8 were investigated in media containing varying concentrations of organic solvents and aqueous hydrofluoric acid. The determination of the distribution coefficients was carried out in 0·15–1·2 M hydrofluoric acid solutions containing 0–90% of the organic solvents methanol, ethanol, n-propanol, isopropanol, methyl glycol, acetone, tetrahydrofuran, and acetic acid. Based on these distribution data the possibilities of separations of the various elements are indicated and discussed.

In previous papers we have described the cation-exchange behaviour of numerous elements in mixed aqueous–organic solvent media containing either hydrochloric acid[1] or nitric acid,[2] Dowex 50 ×8 being used as the cation-exchange resin. The present investigations have been performed by employing the same resin and the same organic solvents but in media containing hydrofluoric acid, so that the data presented in these three papers can be readily compared and evaluated.

No attempt has so far been made to investigate systematically the broad field of mixed aqueous–organic solvent media containing hydrofluoric acid. Not even scattered information is available concerning the cation-exchange behaviour of elements in hydrofluoric acid–organic solvent media. Therefore the research work presented in this paper was performed, using the most frequently employed cation-exchange resin Dowex 50 in mixtures of 8 organic solvents containing hydrofluoric acid. For this purpose the effect of increasing concentration of organic solvent from 0 to 90% in solutions with a constant overall acidity of 0·6M hydrofluoric acid, and the effect of acidity ranging from 0·15 to 1·2M at the constant concentration of 90% of organic solvent were investigated by measuring the distribution coefficients in these media. From the distribution coefficients thus obtained, the possibilities of separating the elements investigated from one another are indicated and discussed.

EXPERIMENTAL

Reagents

Ion-exchange resin. The air-dried strongly acidic cation-exchanger Dowex 50 ×8(100–200 mesh, hydrogen form) was used for the batch and column experiments.

Standard solutions. These solutions were prepared by dissolving the hydroxides, oxides or carbonates of the following metal ions, in an excess of hydrofluoric acid: UO_2(II), Ti(IV), Zr(IV), V(V), Mo(VI), Fe(III), Zn(II), Cd(II), Cu(II), Mn(II), Co(II) and Ni(II). After evaporation to dryness the resulting fluorides were dissolved in 3, 6, or 12M hydrofluoric acid to give solutions containing 10 mg of the element per ml. Tracer amounts of Nb(V), Ta(V) and Pa(V) were used to prepare standard solutions with the same acidities.

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Solvents. The reagent-grade pure organic solvents used were methanol, ethanol, n-propanol, isopropanol, methyl glycol*, acetic acid, tetrahydrofuran and acetone.

Determination of the various elements

All of the bivalent elements, iron(III) and zirconium were determined titrimetrically, by suitable chelatometric methods with EDTA (disodium salt) as the titrant. Fluoride ion was masked with boric acid. For the determination of molybdenum(VI) a method was used which is based on precipitation titration with standard lead nitrate as the titrant and with PAR (4-pyridyl-2-azoresorcinol) as the indicator. Uranium was determined fluorimetrically and vanadium by visual colorimetry.

Niobium, tantalum and protactinium were determined by measuring the radioactivity emitted by their isotopes niobium-94, tantalum-82 and protactinium-233, which have half lives of 2 × 10^4 yr, 115 days and 27 days respectively. The measurements were made with a scintillation counter.

Titanium was determined spectrophotometrically by the well-known peroxide method.

Determination of distribution coefficients

The weight distribution coefficients of all elements except vanadium were determined by using the batch equilibrium method (batch method) described in earlier publications.[1,2] The distribution coefficients of vanadium were determined by using the column method.[2]

RESULTS AND DISCUSSION

In Tables I–XVII the metal ions are arranged in the same order. In many cases the solubility of several of the metal fluorides (especially those of the bivalent metal ions Zn, Cd, Cu, Mn, Co and Ni) in the various hydrofluoric acid–organic solvent mixtures has been found to be very low so that a determination of the distribution coefficients of these elements was not possible. In these instances the Tables do not list the distribution coefficients, instead the abbreviation "ppt" (for precipitation) has been put, although it has been shown in several cases that, under these conditions of low solubility of the fluorides, the distribution values are of the order of $>10^3$.

Table I.—Distribution coefficients in aqueous methanolic 0·6*M* hydrofluoric acid

Ion	Methanol concn., %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	<1	3	190	156
Ti(IV)	<1	2	3	1	1	1
Zr(IV)	<1	<1	1	2·3	5·2	3·5
V(V)	2	3	3	4	4	3
Nb(V), Ta(V), Pa(V)	<1	<1	<1	<1	<1	<1
Mo(VI)	<1	1	1·5	1·7	2	3·3
Fe(III)	<1	3·3	7·2	25·3	87·5	266
Zn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt
Cd(II), Cu(II), Mn(II), Co(II), Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

Uranium(VI)

From the distribution values of uranium shown in Tables I–VIII it is seen that the adsorption of this element invariably increases with an increase of the amount of the non-aqueous component of the mixtures. This increase is most pronounced in the acetone system (see Table VIII) in which a maximum distribution coefficient of 4 × 10^3 is reached in the 90% acetone–10% 6*M* hydrofluoric acid medium. The adsorption of uranium in this as well as in all other media is also increased with a

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* *i.e.*, the monomethyl ether of ethylene glycol, $CH_3—O—CH_2—CH_2OH$.

TABLE II.—DISTRIBUTION COEFFICIENTS IN AQUEOUS ETHANOLIC 0·6*M* HYDROFLUORIC ACID

Ion	Ethanol concn., %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	<1	8·8	29	131
Ti(IV)	<1	3	4	1	1	1
Zr(IV)	<1	<1	1·2	3·3	5·8	6·1
V(V)	2	3	4	4	5	4
Nb(V), Ta(V), Pa(V)	<1	<1	<1	<1	<1	<1
Mo(VI)	<1	1·2	1·8	2·2	3·6	5·5
Fe(III)	<1	4·2	8·7	33·8	123	ppt
Zn(II), Cd(II), Cu(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt
Mn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt	ppt
Co(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt
Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

TABLE III.—DISTRIBUTION COEFFICIENTS IN AQUEOUS n-PROPANOLIC 0·6*M* HYDROFLUORIC ACID

Ion	n-Propanol concn., %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	<1	<1	14	133
Ti(IV)	<1	2	3	2	1	<1
Zr(IV)	<1	<1	1·5	3·6	6·2	6·7
V(V)	2	2	2	3	3	3
Nb(V), Ta(V), Pa(V)	<1	<1	<1	<1	<1	<1
Mo(VI)	<1	1·4	2·1	3·2	4·1	6·2
Fe(III)	<1	2·4	7·8	23	267	ppt
Zn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt	ppt
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt
Cu(II), Mn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt	ppt
Co(II), Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt

TABLE IV.—DISTRIBUTION COEFFICIENTS IN AQUEOUS ISOPROPANOLIC 0·6*M* HYDROFLUORIC ACID

Ion	Isopropanol concn., %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	1·3	2·3	67	505
Ti(IV)	<1	3	4	2	1	<1
Zr(IV)	<1	<1	1·8	3·8	6·3	6·5
V(V)	2	2	3	4	4	4
Nb(V), Ta(V), Pa(V)	<1	<1	<1	<1	<1	<1
Mo(VI)	<1	1·5	2·4	3·6	4·8	6·4
Fe(III)	<1	2·6	10	43	ppt	ppt
Zn(II), Cd(II), Cu(II), Mn(II), Co(II), Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt	ppt

TABLE V.—DISTRIBUTION COEFFICIENTS IN 0·6*M* HYDROFLUORIC ACID IN AQUEOUS METHYL GLYCOL SOLUTION

Ion	Methyl glycol concn., %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	<1	3·8	102	628
Ti(IV)	<1	1	2	1	<1	1
Zr(IV)	<1	<1	2·1	4·2	7·5	7·7
V(V)	2	3	5	6	4	3
Nb(V)	<1	1·2	1	<1	<1	<1
Ta(V), Pa(V)	<1	<1	<1	<1	<1	<1
Mo(VI)	<1	1·7	2·7	4·1	5·6	7·2
Fe(III)	<1	3	13	73	840	ppt
Zn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt	$>10^3$
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt	ppt
Cu(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt
Mn(II), Co(II), Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

TABLE VI.—DISTRIBUTION COEFFICIENTS IN 0·6*M* HYDROFLUORIC ACID IN AQUEOUS ACETIC ACID

Ion	Acetic acid concn., %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	<1	<1	24	160
Ti(IV), Zr(IV)	<1	<1	<1	<1	<1	<1
V(V)	2	2	2	2	2	2
Nb(V), Ta(V), Pa(V)	<1	<1	<1	<1	<1	<1
Mo(VI)	<1	<1	1·1	1·2	1·4	1·5
Fe(III)	<1	1·8	4·5	9·6	24	ppt
Zn(II), Cd(II), Cu(II), Mn(II), Co(II), Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

TABLE VII.—DISTRIBUTION COEFFICIENTS IN 0·6*M* HYDROFLUORIC ACID IN AQUEOUS TETRAHYDROFURAN

Ion	Tetrahydrofuran concn., %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	<1	<1	67	515
Ti(IV)	<1	<1	<1	<1	<1	<1
Zr(IV)	<1	<1	1·4	3·5	6·7	7·2
V(V)	2	2	2	3	3	2
Nb(V)	<1	1·7	1	<1	<1	<1
Ta(V), Pa(V)	<1	<1	<1	<1	<1	<1
Mo(VI)	<1	1·3	2·2	3·5	5·2	5·8
Fe(III)	<1	3	17·4	82	ppt	ppt
Zn(II), Cd(II), Cu(II), Mn(II), Co(II), Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt	ppt

Table VIII.—Distribution coefficients in 0·6*M* hydrofluoric acid in aqueous acetone

Ion	Acetone concn., %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	10	18	39	4000
Ti(IV)	<1	<1	<1	<1	1	1
Zr(IV)	<1	<1	1·1	2·5	5·6	6·8
V(V)	2	3	4	6	8	5
Nb(V)	<1	1	1·3	1	<1	<1
Ta(V), Pa(V)	<1	<1	<1	<1	<1	<1
Mo(VI)	<1	1·1	1·6	2·3	4·7	5·6
Fe(III)	<1	4·2	25	230	ppt	ppt
Zn(II), Cd(II), Cu(II), Mn(II), Co(II), Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt	ppt

Table IX.—Distribution coefficients in 90% methanol mixtures containing 10% of hydrofluoric acid of varied molarity

Ion	Final HF concn., *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	1350	665	156	82	71
Ti(IV)	3	1	1	<1	<1
Zr(IV)	10·4	6·8	3·5	1·4	<1
V(V)	11	8	3	2	<1
Nb(V), Ta(V), Pa(V)	<1	<1	<1	<1	<1
Mo(VI)	6·4	4·2	3·3	1·2	1
Fe(III)	$>10^3$	500	266	85	59
Zn(II)	ppt	ppt	ppt	$>10^3$	$>10^3$
Cd(II), Cu(II), Mn(II), Co(II), Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

Table X.—Distribution coefficients in 90% ethanol mixtures containing 10% of hydrofluoric acid of varied molarity

Ion	Final HF concn., *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	1700	530	131	59	49
Ti(IV)	4	1	1	<1	<1
Zr(IV)	12·5	8·2	6·1	1·7	<1
V(V)	13	10	4	2	<1
Nb(V), Ta(V), Pa(V)	<1	<1	<1	<1	<1
Mo(VI)	7·8	6·2	5·5	2·6	1·3
Fe(III), Zn(II), Cd(II), Cu(II), Mn(II), Co(II)	ppt	ppt	ppt	ppt	ppt
Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

TABLE XI.—DISTRIBUTION COEFFICIENTS IN 90% n-PROPANOL MIXTURES CONTAINING 10% OF HYDROFLUORIC ACID OF VARIED MOLARITY

Ion	Final HF concn., *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	1450	550	133	76	57
Ti(IV)	2	1	<1	<1	<1
Zr(IV)	14·3	9·5	6·7	2·2	<1
V(V)	16	6	3	2	<1
Nb(V), Ta(V), Pa(V)	<1	<1	<1	<1	<1
Mo(VI)	8·4	6·8	6·2	2·8	1·2
Fe(III), Zn(II), Cd(II), Cu(II), Mn(II), Co(II), Ni(II)	ppt	ppt	ppt	ppt	ppt

TABLE XII.—DISTRIBUTION COEFFICIENTS IN 90% ISOPROPANOL MIXTURES CONTAINING 10% OF HYDROFLUORIC ACID OF VARIED MOLARITY

Ion	Final HF concn., *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	4000	2000	505	320	230
Ti(IV)	2	1	<1	<1	<1
Zr(IV)	13·6	8·8	6·5	2	<1
V(V)	9	4	3	2	<1
Nb(V), Ta(V), Pa(V)	<1	<1	<1	<1	<1
Mo(VI)	8·8	7·1	6·4	3·1	1·4
Fe(III), Zn(II), Cd(II), Cu(II), Mn(II), Co(II), Ni(II)	ppt	ppt	ppt	ppt	ppt

TABLE XIII.—DISTRIBUTION COEFFICIENTS IN 90% METHYL GLYCOL MIXTURES CONTAINING 10% OF HYDROFLUORIC ACID OF VARIED MOLARITY

Ion	Final HF concn., *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	3450	2200	628	475	332
Ti(IV)	4	2	1	<1	<1
Zr(IV)	17·5	10·8	7·7	2·6	<1
V(V)	12	7	5	2	<1
Nb(V), Ta(V), Pa(V)	<1	<1	<1	<1	<1
Mo(VI)	12·5	8·7	7·2	3·8	1·7
Fe(III)	ppt	ppt	ppt	ppt	ppt
Zn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cd(II)	ppt	ppt	ppt	ppt	ppt
Cu(II)	ppt	ppt	ppt	ppt	$>10^3$
Mn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Co(II)	ppt	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

Table XIV.—Distribution coefficients in 90% acetic acid mixtures containing 10% of hydrofluoric acid of varied molarity

Ion	Final HF concn., *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	850	440	160	104	88
Ti(IV), Zr(IV)	<1	<1	<1	<1	<1
V(V)	2	2	2	2	<1
Nb(V), Ta(V), Pa(V)	<1	<1	<1	<1	<1
Mo(VI)	3·8	2·9	1·5	1·0	<1
Fe(III)	ppt	ppt	ppt	ppt	ppt
Zn(II), Cd(II), Cu(II), Mn(II), Co(II), Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

Table XV.—Distribution coefficients in 90% tetrahydrofuran mixtures containing 10% of hydrofluoric acid of varied molarity

Ion	Final HF concn., *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	3140	1930	515	400	300
Ti(IV)	<1	<1	<1	<1	<1
Zr(IV)	12·8	8·4	7·2	3·6	2·5
V(V)	4	2	2	1	<1
Nb(V), Ta(V), Pa(V)	<1	<1	<1	<1	<1
Mo(VI)	10·6	7·2	5·8	3·6	1·5
Fe(III), Zn(II), Cd(II), Cu(II) Mn(II), Co(II), Ni(II)	ppt	ppt	ppt	ppt	ppt

Table XVI.—Distribution coefficients in 90% acetone mixtures containing 10% of hydrofluoric acid of varied molarity

Ion	Final HF concn., *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	10^4	7800	4000	3000	2840
Ti(IV)	3	2	1	<1	<1
Zr(IV)	10·7	7·3	6·8	2·1	1·3
V(V)	25	12	5	2	<1
Nb(V), Ta(V), Pa(V)	<1	<1	<1	<1	<1
Mo(VI)	9·5	7·0	5·6	2·2	<1
Fe(III), Zn(II), Cd(II), Cu(II), Mn(II), Co(II), Ni(II)	ppt	ppt	ppt	ppt	ppt

decrease of the overall hydrofluoric acid concentration (see Tables IX–XVI). This behaviour does not occur in pure aqueous hydrofluoric acid solutions of varied molarity; in these the distribution coefficient of uranium is invariably lower than unity irrespective of the hydrofluoric acid concentration of the media (see Table XVII). The same behaviour is shown by Ti, Zr, V, Nb, Ta and Pa so that these elements cannot be separated from uranium in the acidity range from 0·15 to 1·2*M* hydrofluoric

TABLE XVII.—DISTRIBUTION COEFFICIENTS IN HYDROFLUORIC ACID OF VARIED MOLARITY

Ion	Final HF concn., M				
	0·15	0·3	0·6	0·9	1·2
UO_2(II), Ti(IV) Zr(IV)	<1	<1	<1	<1	<1
V(V)	2	2	2	<1	<1
Nb(V), Ta(V), Pa(V)	<1	<1	<1	<1	<1
Mo(VI)	3·5	1·2	<1	<1	<1
Fe(III)	25	5·4	<1	<1	<1
Zn(II), Cd(II), Cu(II), Mn(II), Co(II), Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

acid, although separations of uranium from molybdenum and iron would be feasible in 0·15–0·3M hydrofluoric acid because of the difference in the distribution coefficients (see Table XVII). Furthermore a separation of uranium together with the elements mentioned above is possible from the bivalent metal ions listed in Table XVII which show distribution values of the order of $>10^3$ in pure aqueous hydrofluoric acid solutions.

With the use of 90% organic solvent–10% hydrofluoric acid solutions, however, uranium can be separated from Ti, Zr, V, Nb, Ta, Pa and Mo at all acid concentrations shown in Tables IX–XVI. No separation of uranium in these media can be achieved from the bivalent metal ions. Consequently a scheme for the separation of uranium from most of the elements listed in Tables I–XVII would involve the following two steps: (1) adsorption of Zn, Cu, Cd, Mn, Co and Ni from 1·2M hydrofluoric acid (see Table XVII; this separates uranium from the bivalent ions but not from Ti, Zr, V, Nb, Ta, Pa and Mo which pass into the effluent together with uranium); (2) adsorption of uranium from, *e.g.*, 90% acetone–10% 12M hydrofluoric acid (see Table XVI; this separates uranium from Ti, Zr, V, Nb, Ta, Pa and Mo). For the elution of adsorbed uranium 0·15–1·2M hydrofluoric acid may be employed.

Titanium(IV) and zirconium(IV)

While these elements are not retained on Dowex 50 from pure aqueous hydrofluoric acid solutions of varied molarity (see Table XVII), some adsorption is observed in the mixed aqueous–organic systems shown in Tables I–XVI. In the latter media the adsorbability of titanium is usually lower than that of zirconium, and when the concentration of the nonaqueous component is increased the distribution coefficient of titanium reaches a maximum at 40% organic solvent concentration. This is true for the systems containing methanol, ethanol, n-propanol, isopropanol and methyl glycol (see Tables I–V) but not for those shown in Tables V–VIII in which titanium shows the same behaviour as in pure aqueous hydrofluoric acid solutions, *i.e.*, no adsorption of titanium is observed.

In the case of zirconium the adsorption increases rather regularly with an increase of the concentration of the organic components of the mixtures (see Tables I–V, VII and VIII). Only in acetic acid–0·6M hydrofluoric acid mixtures (see Table VI) does zirconium show the same adsorption behaviour as in pure aqueous hydrofluoric acid solutions (compare data of Table VI with those shown in Table XVII).

With an increase of the hydrofluoric acid concentration in the mixed aqueous–organic systems the distribution coefficients of both titanium and zirconium invariably decrease (see Tables IX–XVI). Because the distribution coefficients of titanium and zirconium in several of these systems are sufficiently different from each other, separations of these elements in some of the mixtures should be possible.

Vanadium(V), niobium(V), tantalum(V), protactinium(V) and molybdenum(VI)

Vanadium and molybdenum are slightly adsorbed from some of the systems shown in Tables I–XVII, but niobium, tantalum and protactinium are very little if at all retained by the resin. Therefore separations of these elements from one another cannot be achieved though they can be readily separated from uranium, iron(III) and bivalent metal ions. Separation of niobium from zirconium is possible in several media.

Iron(III) and bivalent metal ions

In the mixed aqueous–organic media shown in Tables I–XVI, iron(III) shows an adsorption behaviour which is similar to that of uranium(VI). Consequently separations of these two elements cannot readily be achieved in most media, though iron is separable from the bivalent metal ions as well as from Ti, Zr, V, Nb, Ta, Pa and Mo.

In all the media investigated all of the bivalent metal ions, *i.e.*, Zn, Cd, Cu, Mn, Co and Ni, have distribution coefficients which are of the order of $>10^3$ (see Tables I–XVII) so that separations from each other are impossible. They can only be separated from the slightly adsorbed elements. On the basis of these results it can be concluded that the bivalent metal ions do not form anionic fluoride complexes which would prevent their retention by Dowex 50. On the other hand all of the other metal ions investigated do form such complexes, with stabilities which vary with the different conditions employed.

Zusammenfassung—Die charakteristischen Kationenaustauscheigenschaften von 15 Elementen mit dem stark sauren Kationenaustauscherharz Dowex 50 ×8 wurden in Medien untersucht, die wechselnde Konzentrationen organischer Lösungsmittel und wäßrige Flußsäure enthielten. Die Verteilungskoeffizienten wurden in 0,15–1,2 *M* flußsauren Lösungen bestimmt die 0–90% der organischen Lösungsmittel Methanol, Äthanol, n-Propanol, Isopropanol. Methylglykol, Aceton, Tetrahydrofuran und Essigsäure ethielten. Auf Grund dieser Verteilungsdaten werden Möglichkeiten von Trennungen der verschiedenen Elemente voneinander angegeben und diskutiert.

Résumé—On a étudié les caractéristiques d'échange de cations de 15 éléments avec la résine échangeuse de cations fortement acide Dowex 50 × 8 dans des milieux contenant des concentrations variables de solvants organiques et d'acide fluorhydrique aqueux. La détermination des coefficients de partage a été menée dans des solutions 0,15–1,2*M* en acide fluorhydrique contenant 0–90% des solvants organiques méthanol, éthanol, n-propanol, isopropanol, méthylglycol, acétone, tétrahydrofuran et acide acétique. En se basant sur ces données de partage, on montre les possibilités de séparations des divers éléments et en discute.

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SHORT COMMUNICATIONS

Determination of moisture on thorium dioxide by a coulometric electrolytic measurement with electronic integration

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METHODS available for the determination of moisture sorbed on solids range from indirect measurements, such as loss on drying, to direct measurements such as the absorption of evolved water on magnesium perchlorate and the Karl Fisher titration.[1,2] The choice of method is generally dictated by the quantity of moisture present, its affinity for the solid, and the sample composition. In the case of sintered thorium dioxide, the primary consideration is the ability to measure accurately very small quantities of water.

The Consolidated Electrodynamics Corporation, Pasadena, California, markets a Solids Moisture Analyser, Type 26-321A, based on the coulometric electrolytic principle. An accuracy of ±20 μg of water or ±2% of the final reading, whichever is larger, is claimed. The desire for greater precision and accuracy when the amount of water available for measurement is small, led to development of the methodology and instrumentation described herein. The method should be readily adaptable to many materials other than thorium dioxide.

EXPERIMENTAL

Apparatus

Beckman electrolytic hygrometer model 17901.

Dymec voltage-to-frequency converter model 5207-1.

Beckman Berkeley EPUT meter model 7151-6.

Honeywell Electronik recorder model 19 (or an equivalent instrument).

A 6-in. tube furnace (1-in. diameter) with a variable autotransformer for temperature control. The furnace should be so constructed that the upper half can be raised if rapid cooling of the tube is desired.

The heating tube is 25-mm Vycor and 11 in. long. The male part of a 35/20 ball and socket joint is sealed to one end of the tube to serve as a sample port for the introduction of platinum boats (3 × ⅜ × ⅜ in.) holding the text specimens. An 8-mm dia. side-arm, 2½ in. from the sample port, allows the introduction of the sweep gas into the heating tube and at the same time serves as a back-flushing system which keeps the tube dry when opened for specimen introduction. The tube is also fitted with an exit side-arm and thermocouple well. As indicated in Fig. 1, the side-arms are fitted with 12/5 ball and socket joints. The joints permit union with steel joints which are in turn soldered to copper tubing. A stop-cock is located upstream from the heating tube; this stop-cock permits regulation of the sweep gas during specimen loading.

Procedure

After assembly of the components as illustrated in Fig. 1, the system is dried with argon sweep gas (moisture content less than 1·0 ppm) maintained at 14 psig. The gas flow through the hygrometer is regulated to 100 cm^3/min.

Results reported in this paper were obtained with the following instrument settings.

1. Hygrometer meter selection switch—1000; the recorder and Dymec voltage-to-frequency converter were connected to the 10-mV taps on the hygrometer terminal strip.
2. Voltage range on the V–F converter—0 to 0·1 V.
3. Digital divider on the EPUT meter—10.

With a dry system, the background count rate on the EPUT meter should not exceed several counts/min. All components should be in operation when the heating tube is opened and a specimen is inserted. Heating is begun immediately after the tube is resealed. The specimen must be heated at such a rate that the resulting moisture in the sweep gas never exceeds the operating capacity of the

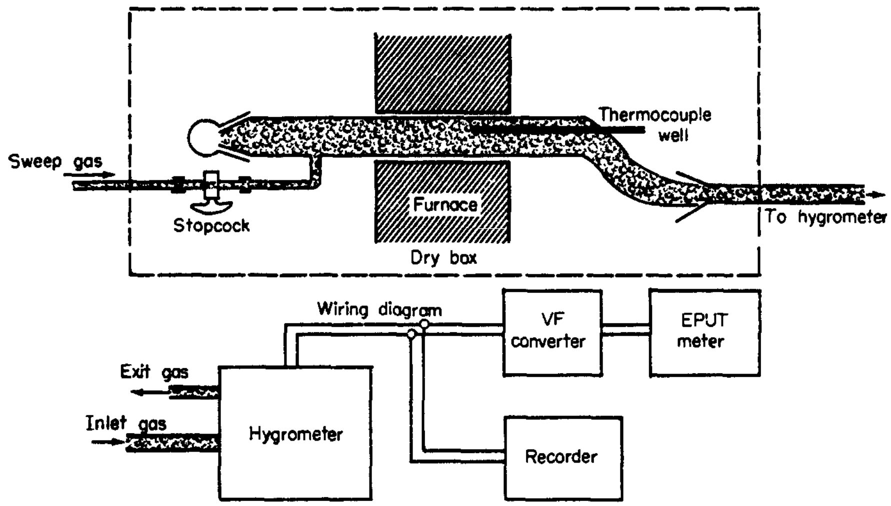

FIG. 1.—Apparatus for determining moisture on solids.

hygrometer—1000 ppm. When the desired maximum temperature is reached, it is maintained until the count rate on the EPUT meter diminishes to background. The time required for a determination is 20–30 min.

RESULTS

The assembled instrumentation was calibrated with sodium tartrate dihydrate (15·66% water) and barium chloride dihydrate (14·75% water). Prior to their use, the water content of each was verified by drying weighed amounts at 150°. The results of this calibration are given in Table I.

A procedure similar to that used for instrumentation calibration was employed in the analysis of a sintered thorium dioxide specimen. Typical results are shown in Table II.

TABLE I.—COUNTS PER MICROGRAM OF WATER OBTAINED FROM SODIUM TARTRATE DIHYDRATE AND BARIUM CHLORIDE DIHYDRATE*

Sample	Weight, *mg*	Water calculated, *μg*	Total count†	Counts/μg H_2O
$Na_2C_4H_4O_6 \cdot 2H_2O$	0·186	29	2140	74
	0·701	110	8150	74
	1·206	189	13730	73
	1·401	219	15850	72
	1·677	263	19500	74
$BaCl_2 \cdot 2H_2O$	0·211	31	2350	76
	1·030	152	11380	75
	2·255	333	25600	77
	2·293	338	26000	77

* Furnace temperature 150°C.

† Adjusted to eliminate the cumulative background count; the blank for the platinum boat was less than 100 counts in 20 min (equivalent to 1·3 μg of water) and no correction was applied for it.

TABLE II.—DETERMINATION OF WATER SORBED ON SINTERED THORIUM DIOXIDE

Sample	Weight, *g*	Treatment	Water* *μg*	Water* *ppm*
1	7·8952	As received	158	20
2	3·5725	As received	72	20
3	2·2475	Ignited at 900°C—placed in reaction tube while still hot	<1·0	<0·5
4	7·8629	Ignited at 900°C—cooled in desiccator (drierite)	141	18
5	6·0794	Ignited at 900°C followed by exposure to lab. atmosphere for 1 day	115	19
6	6·9287	Ignited at 900°C followed by exposure to lab. atmosphere for 14 days	147	21

* Based on 75 counts/μg H_2O; furnace temperature 350°C.

DISCUSSION

Performance specifications of the various components employed in this determination, used in conjunction with the instrument settings set forth in this paper, permit a calculation of the theoretical counts /μg of water. The essentials of this calculation are as follows.

Assume sweep gas contains 1000 ppm moisture and flows for 1 min.

(*a*) With a flow-rate of 100 cm^3/min, 0·1 cm^3 of $H_2O_{(g)}$ or 80 μg of $H_2O_{(l)}$ will enter the hygrometer.

(*b*) At full-scale deflection (1000 ppm moisture), the hygrometer output is 10 mV. Thus the input into the V–F converter is 10 mV.

(*c*) The V–F converter produces 10,000 output pulses/sec for 0·1 V input. A 10 mV input will thus produce 1000 output pulses/sec or 60,000 pulses/min.

(*d*) With the digital divider on the EPUT meter set at 10, every tenth pulse is counted. Thus 60,000 pulses/min will produce 6000 counts/min.

(*e*) Therefore, 6000 counts/min represents 80 μg of water passing through the hygrometer in 1 min, and 75 counts will represent 1 μg of water.

The average number of counts/μg of water obtained (Table I) is 74. It is the authors' opinion that the spread in values (±5%) shown in Table I can be attributed to weighing (standard samples restricted to 0·1–2·5 mg) and to transfer errors. If this is the case, better accuracy will be attained when larger samples (thorium dioxide) are analysed. Unfortunately, we do not possess standards that permit us to test this belief.

The moisture values presented in Table II indicate that (*a*) the method yields excellent precision on thorium dioxide, (*b*) the sample of thorium dioxide selected for testing did not readily sorb moisture from the air, and (*c*) special handling precautions for thorium dioxide samples in the laboratory are not necessary unless there is an interest in very low moisture content (in this respect, the entire heating chamber is readily adaptable to a dry box enclosure).

A recorder was employed to provide a profile of the rate at which moisture is released from a specimen (*vs.* temperature and time). For routine analyses, the recorder can be left out.

The flexibility of the components comprising the total moisture instrumentation is demonstrated in the calculation of the theoretical counts/μg of water. The calculation indicates that by use of other instrument settings, the apparent sensitivity of the moisture measurement can be increased or decreased.

While the instrumentation was designed specifically to measure moisture on sintered thorium dioxide, its applicability to other solid materials is self-evident. For example, the method has been applied to the determination of moisture on uranium oxide. In addition, with hydrogen used as a sweep gas, the instrumentation has been applied to the measurement of oxygen-to-uranium ratios in UO_{2+x}. The ratios are in agreement with those obtained by other techniques.

The proper functioning of the phosphorus pentoxide desiccant in the electrolytic cell is absolutely essential to this moisture procedure. Beckman literature indicates that the following materials prevent proper moisture measurements; alcohols, ammonia, amines, basic gases, unsaturated hydrocarbons, corrosive gases and dust particles. Consequently, solids which will yield these substances on heating are not suitable for this type of moisture analysis.

Whenever a heating procedure is used to remove moisture sorbed on a specimen, it is well to bear in mind that results may be distorted if the specimen undergoes decomposition or a reaction occurs between the specimen and a temporarily moist atmosphere.

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Summary—The coulometric electrolytic principle is utilized for the measurement of moisture sorbed on sintered thorium dioxide. Moisture is removed from the sample by heating and is swept by dry argon gas through a hygrometer. The resulting hygrometer output is converted into frequency pulses and counted cumulatively. The instrument is calibrated by use of standard hydrated chemicals. The number of counts/μg of water obtained from standards compares favourably with the theoretical number of counts/μg calculated from performance specifications of the components employed. The error is $<5\%$ for 1–350 μg of water. A high sensitivity and low operating blank recommends application of this method to materials other than thorium dioxide, having very low moisture contents.

Résumé—On utilise le principe coulométrique électrolytique pour la mesure de l'humidité sorbée sur le bioxyde de thorium fritté. L'humidité est éliminée de l'échantillon par chauffage et est balayée par de l'argon sec à travers un hygromètre. Le signal résultant de l'hygromètre est converti en impulsions de fréquence et compté cumulativement. L'instrument est calibré par l'emploi de produits chimiques hydratés étalons. La valeur du comptage/μg d'eau obtenue à partir des étalons est favorablement comparable à la valeur théorique du comptage/μg calculée à partir des spécifications de rendement des composés employés. L'erreur est $<5\%$ pour 1–350 μg d'eau. Une haute sensibilité et un témoin faible recommandent l'application de cette méthode à des substances, autres que le bioxyde de thorium, ayant une très faible teneur en humidité.

Zusammenfassung—Das Prinzip der coulometrischen Elektrolyse wird für die Messung an gesintertem Thoriumdioxid adsorbierter Feuchtigkeit verwendet. Die Feuchtigkeit wird durch Erhitzen aus der Probe entfernt und durch trockenes Argon durch ein Hygrometer gespült. Die Anzeige am Hygrometerausgang wird in Frequenzimpulse umgewandelt und integrierend gezählt. Das Instrument wird mit standardisierten Hydraten geeicht. Die Anzahl von Zählimpulsen pro μg Wasser aus Standards stimmt gut mit dem Erwartungswert nach den angegebenen Betriebsdaten der verwendeten Bauteile überein. Der Fehler liegt für 1–350 μg Wasser unter 5%. Hohe Empfindlichkeit und geringer Blindwert empfehlen das Verfahren auch bei anderen Materialien mit sehr geringem Feuchtigkeitsgehalt außer Thoriumdioxid.

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Determination of critical micelle concentration of non-ionic surfactants by electrocapillary curves

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SURFACE active agents, even in trace quantities, can have a remarkable influence on electrode processes. Adsorption of these substances at the electrode surface may decrease the limiting currents, shift the half-wave potentials, and in some cases obliterate the entire wave, and may also cause minima or deceiving split waves.

Adsorption of highly surface-active organic compounds also influences the conventional polarographic drop-time measurements. This has recently been demonstrated by Barradas and Kimmerle[1] who obtained electrocapillary curves in the potential range of +0·1 to −1·0 V (*vs.* S.C.E.) for 0·1*M* potassium chloride solutions of the organic additive from $3·0 \times 10^{-5}$ to $2·1 \times 10^{-4}M$ in concentration.

We have made use of this effect to determine the critical micelle concentration (C.M.C.) of some non-ionic surfactants, *viz.*, Nonidet P40, Nonidet P42 and Nonex 501. The C.M.C. values so obtained have been compared with the values obtained by the maximum-suppression, surface tension and iodine-solubilization methods.

EXPERIMENTAL

Non-ionic surfactants *viz.* Nonidet P40 (polyethylene oxide condensate 100%), Nonidet P42 (condensation product of dioctyl phenol and ethylene oxide) and Nonex 501 (methoxy-polyethylene glycol laurate) were B.D.H. products. Other reagents used were either analytical reagent grade or chemically pure products. Doubly distilled water was used for preparing the solutions.

A Heyrovský polarograph Lp 55A with a Pye Scalamp galvanometer was used for polarographic and electrocapillary measurements. The solutions were de-aerated by bubbling hydrogen through them in H-type polarographic cells. At least 20 drops were counted and the drop-time was measured with a precision stop-watch. Each set of measurements at a constant potential was repeated three times. The electrocapillary data were obtained from 0·0 to −1·2 V *vs.* S.C.E. (Fig. 1). The temperature was maintained at 25° ± 0·1°. Drop-times were plotted *vs.* surfactant concentration (Figs. 2–4). The C.M.C. value was obtained by finding the surfactant concentration at the intersection of the extrapolations of the steep part of the curve and of the final horizontal portion.

Maximum-suppression method

Polarographic measurements were made by introducing a known volume of the metal salt solution (0·01*M* nickel or 0·005*M* cobalt) into the polarographic cell, adding the supporting electrolyte (1*M* potassium chloride) and making up the total volume to 10 ml. The solution was de-aerated and the polarogram taken, then the process was repeated in the presence of the non-ionic surfactant, the C.M.C. of which was to be determined. An increasing amount of the surfactant was added until the maximum was completely eliminated. The details of the method are described elsewhere.[2]

Iodine-solubilization method[3]

For the determination of the C.M.C. by this method, absorption measurements were made with a Bausch and Lomb Spectronic-20.

A stock solution of iodine was prepared, containing 127 mg/l., and diluted with different amounts of surfactants. The spectrophotometric measurements were made at a wavelength of 360 mμ (iodine–micelle complex absorption maximum). It was always found useful to take the reading within an hour of preparation of a solution because of a slow fading of the colour of the iodine–micelle complex.

RESULTS AND DISCUSSION

Figure 1 shows the variation of drop time with concentration of Nonidet P42 from 0·0 to −1·2 V *vs.* the S.C.E. Curve A in Fig. 1 shows the relationship between the electrode potential and the drop time in 0·1*M* potassium chloride. The curve is symmetrical and parabolic, showing specifically no adsorption on the mercury surface. However, with increasing concentration of Nonidet P42, or one of the other two non-ionic surfactants, the electrocapillary maximum (E.C.M.) shifts towards more positive potentials (Fig. 1, curves B to H).

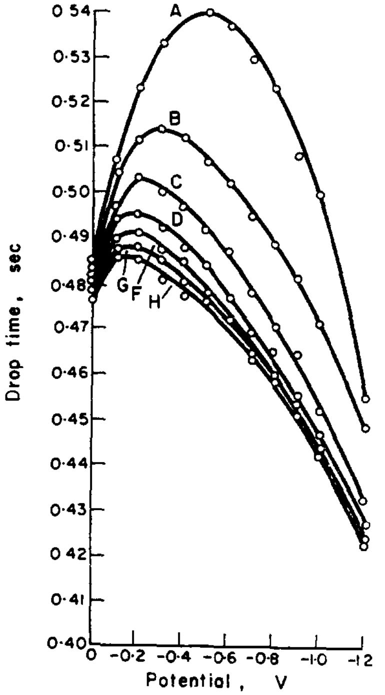

FIG. 1.—Electrocapillary curves for Nonidet P42 in 0·1*M* potassium chloride. Concentration of surfactant: *A*—0·0; *B*—0·02; *C*—0·06; *D*—0·08; *E*—0·10; *F*—0·12; *G*—0·14; *H*—0·16; all in g/l.

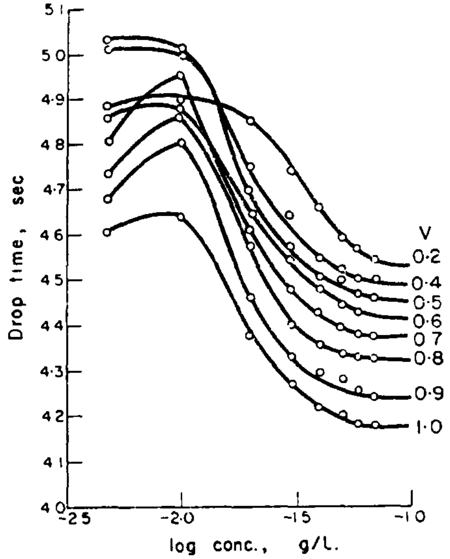

FIG. 3.—Effect of concentration (g/l) of Nonex 501 on drop-time at various potentials.

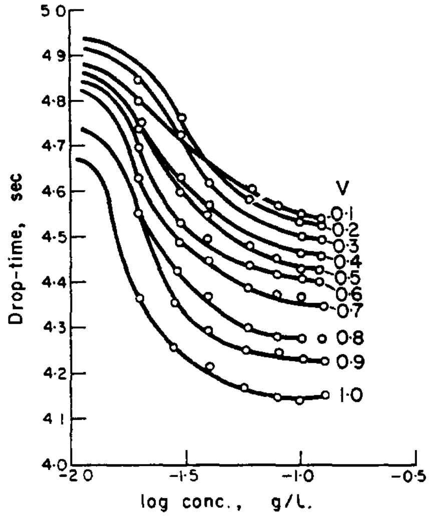

FIG. 2.—Effect of concentration (g/l) of Nonidet P40 no drop-time at various applied potentials.

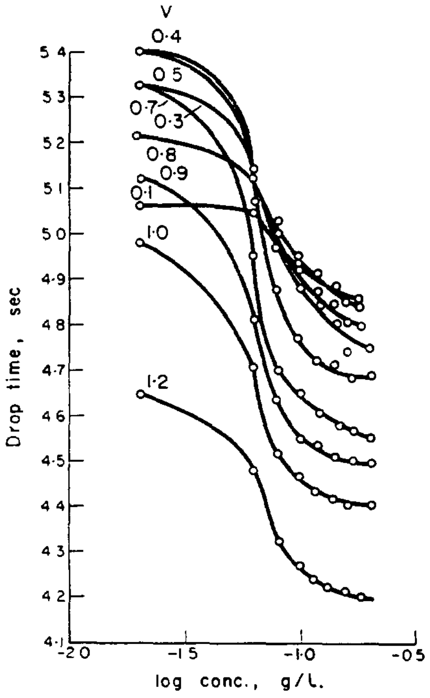

FIG. 4.—Effect of concentration (g/l) of Nonidet P42 on drop-time at various potentials.

TABLE I.—COMPARATIVE C.M.C. VALUES OF NON-IONIC SURFACTANTS

Method	Nonidet P40, *g/l*	Nonex 501, *g/l*	Nonidet P42, *g/l*
1. Electrocapillary method in 0·1*M* KCl	$7{\cdot}6 \times 10^{-2}$	$4{\cdot}7 \times 10^{-2}$	$13{\cdot}8 \times 10^{-2}$
2. Iodine solubilization method in water	$12{\cdot}0 \times 10^{-2}$	$4{\cdot}8 \times 10^{-2}$	$35{\cdot}0 \times 10^{-2}$
3. Surface tension method	$12{\cdot}5 \times 10^{-2}$	$6{\cdot}2 \times 10^{-2}$	$39{\cdot}8 \times 10^{-2}$
4. Polarographic maximum-suppression method			
Co^{2+} in 0·1*M* KCl	$2{\cdot}3 \times 10^{-3}$	$2{\cdot}3 \times 10^{-3}$	$8{\cdot}6 \times 10^{-3}$
Ni^{2+} in 0·1*M* KCl	$3{\cdot}6 \times 10^{-3}$	$2{\cdot}3 \times 10^{-3}$	$11{\cdot}6 \times 10^{-3}$

This shift needs a little explanation since only ionic surfactants are known to effect such a change. With non-electrolytes such as amyl alcohol, no shift of the E.C.M. is observed and only a flattening of the top takes place.[4] A similar behaviour was observed by us with the non-ionic soap, lauric acid diethanolamine condensate.[5] The peculiar behaviour shown by the non-ionic surfactants under investigation can be explained in the light of the model purposed by Barradas and Kimmerle[6] for multilayer adsorption of Triton X-100, Triton X-305 and other similar compounds.

According to them the first adsorbed layer of the non-ionic surfactants extends its contracted "zig-zag" hydrophilic portions towards the solution. A second layer is then assumed to form by intermolecular hydrogen-bonding with another perpendicular array of surfactant molecules, and a third layer is formed by van der Waals attractive forces between similar non-polar ends of the molecules. Further, each compact array of the surfactant molecules may form hydrogen bonds with some water molecules since it is well known that micellar structures of these surfactant molecules are usually hydrated.[7]

Figures 2–4 show plots of drop-time against log of concentration for the potential range −0·1 to 1·0 V. These curves show an initial slow change followed by a sharp decrease in drop-time until a concentration of 10^{-2} g/l is reached, when the curves show signs of flattening out. Since flattening sets in at the same concentration irrespective of the potential applied, this concentration can be taken as the point of incipient micelle formation. The results for the three surfactants are given in Table I.

The C.M.C. values determined by the other three methods (Table I) reveal that the values obtained from the surface tension and iodine-solubilization methods are comparable and lie in almost the same concentration range. The values obtained from the polarographic maximum suppression method, however, vary markedly from those found by the other three methods. This discrepancy may be attributed to the very small amount of non-ionic, as compared with ionic surfactants, required to

TABLE II.—COMPARATIVE C.M.C. VALUES OF ANIONIC SURFACTANTS*

	SPSA, *g/l*	STSA, *g/l*	SXSA, *g/l*
1. Polarographic maximum-suppression method, Ni^{2+} in 0·1*M* KCl	$3{\cdot}6 \times 10^{-2}$	$21{\cdot}2 \times 10^{-2}$	$17{\cdot}0 \times 10^{-2}$
2. pH method (without electrolyte)	$6{\cdot}10 \times 10^{-2}$	$7{\cdot}10 \times 10^{-2}$	$9{\cdot}4 \times 10^{-2}$
3. Conductometric method (without electrolyte)	$18{\cdot}9 \times 10^{-2}$	$22{\cdot}7 \times 10^{-2}$	$25{\cdot}1 \times 10^{-2}$

SPSA = sulphonated phenylstearic acid.
STSA = sulphonated tolylstearic acid.
SXSA = sulphonated xylylstearic acid.
* C.M.C. values taken from Ref. 7.

suppress the maxima with the result that the polarographic measurements fail to give a true measure of the C.M.C. values. Investigations with ionic surfactants[8] give comparable values since much higher concentrations are required for the suppression of the polarographic maxima than with non-ionic surfactants (Table II). It appears, therefore, that the polarographic maximum-suppression method is not suitable for the determination of the C.M.C. of non-ionic surfactants. Instead, the polarographic method based on the shift of electrocapillary curves in the presence of varying concentrations of the surfactant may be fruitfully employed.

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Summary—A method is described for the determination of the critical micelle concentration of non-ionic surfactants by measurement of their effect on the electrocapillary curves for a dropping mercury electrode. The method was compared with the iodine-solubilization, surface tension, and polarographic maximum suppression methods.

Zusammenfassung—Ein Verfahren zur Bestimmung der kritischen Micellkonzentration nichtionischer oberflächenaktiver Substanzen wird angegeben. Dabei wird ihr Einfluß auf die Elektrokapillarkurven einer Quecksilbertropfelektrode gemessen. Das Verfahren wurde mit den Methoden der Jod-Solubilisierung, der Oberflächenspannung und der Unterdrückung polarographischer Maxima verglichen.

Résumé—On décrit une méthode pour la détermination de la concentration critique en micelles de surfactants non ioniques par mesure de leur effet sur les courbes électrocapillaires pour une électrode à goutte de mercure. On a comparé la méthode avec celles de solubilisation de l'iode, de tension superficielle et de suppression du maximum polarographique.

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Carrier-free separation of ^{115m}In from irradiated Cd by solvent extraction with 1-phenyl-3-methyl-4-caproylpyrazolone-5

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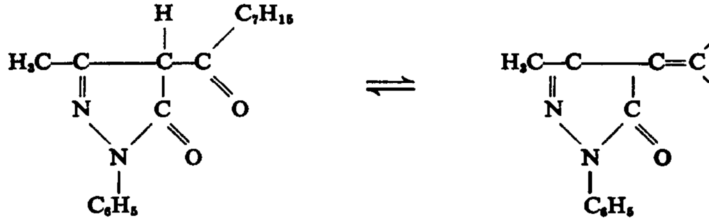
SHORT-LIVED γ-emitting radionuclides milked from longer-lived parent nuclides have found considerable application in biological investigations. Because of their short half-life, such nuclides may be administered in large doses without danger of excessive radiation dosage. Among the most promising systems for scintillographic determinations suggested by Pal *et al.*[1] is ^{115}Cd–^{115m}In. ^{115m}In is administered in the form of labelled compounds. It forms stable chelates with ethylenediaminetetra-acetate (EDTA) or diethylenetriaminepenta-acetate (DTPA). Although ionic indium is one of the most toxic of all metals,[2-4] comparable to uranyl and mercury(II) ions, carrier-free indium may be administered safely to patients. The desirable characteristics which ^{115m}In possesses are a short half-life of 4½ hr, a monoenergetic γ-emission of 335 keV (95%) by isomeric transition[5] and 860 keV (5%) β-emission which does not contribute much to the radiation dosage. Because of its favourable physical, chemical and biological properties, this isotope can be considered as a source of new methods in isotopic diagnostics.[1] Various methods for its production followed by ion-exchange[6,7] and solvent extraction[6,8] techniques have been reported in the literature.

In this paper, a method is presented for milking of ^{115m}In from its parent ^{115}Cd by using 1-phenyl-3-methyl-4-caproylpyrazolone-5 (PMCyP) in an isobutyl methyl ketone (MBIK) and water system. The method of synthesis and the physico-chemical constants of 4-acyl derivatives of 1-phenyl-3-methylpyrazolone-5 as chelating agents have been reported by Jensen.[9,10] Zolotov *et al.*[11-13] have used the 4-benzoyl derivative of 1-phenyl-3-methylpyrazolone-5 for the extraction of Ca, Sr, Sc, Mn, Fe(III), Zr and Pu(IV) from various aqueous media with various solvents, and the 4-caproyl derivative of 1-phenyl-3-methylpyrazolone-5 has been previously used[14-16] for the extraction of ^{54}Mn, ^{58}Co, ^{59}Fe, ^{90}Y, ^{89,90}Sr (from fission products) and ^{115}Cd (from fission products).

We studied the extraction of a large number of elements with PMCyP/IBMK, intending to apply the data obtained to resolve analytical and radiochemical problems. It was found that PMCyP is a very effective extractant.



Keto Enol

PMCyP is a β-diketone and exists in both the keto and the enol form. The yellow-green enol form is obtained by recrystallization from heptane while the colourless keto form is obtained by recrystallization from an ethanol–water mixture. No difference in the behaviour of these two forms was observed. In the present work, the keto form was used. ^{115m}In is obtained by the beta-decay of ^{115}Cd.

EXPERIMENTAL

Apparatus

A Radiometer pH meter PHM 22 was used for pH measurements. Separatory-funnels (25-ml) were used for the separation of phases and ordinary glass tubes were used for manual shaking in the extraction study. In the production procedure, agitation was done with a magnetic stirrer and the whole operation was performed behind lead shielding.

Materials

Preparation of 1-*phenyl*-3-*methyl*-4-*caproylpyrazolone*-5 (PMCyP). Dissolve 1-phenyl-3-methylpyrazolone (17·4 g) in dioxan (50 ml) in a flask equipped with a stirrer, separatory-funnel and reflux condenser, using a very low flame. Add calcium hydroxide (10 g) and then caproyl chloride (10 g) dropwise in 1 min. Stir the mixture, heat it with an infrared lamp and reflux it for 90 min till the yellow calcium complex is formed. Decompose the calcium complex by adding 100 ml of 3*N* hydrochloric acid; cream crystals separate. Recrystallize the crystals from an ethanol-water mixture containing a little hydrochloric acid to destroy any undecomposed calcium complex. The crystals are colourless; yield 83%, m.p. 76°. Use as a 1% solution in isobutyl methyl ketone (IBMK).

All the other reagents were of analytical reagent grade and used without further purification. The radionuclides ^{109}Cd and ^{114m}In used as tracers were prepared locally.

Buffers

Standard buffers of potassium chloride and hydrochloric acid, hydrochloric acid and potassium hydrogen phthalate, sodium hydroxide and potassium hydrogen phthalate, and sodium hydroxide and boric acid were used to cover the pH range 1–10.

Radioassay

The characteristic radiations were measured with an end-window G.M. counter. A β–γ-ionization chamber was used for measuring the final yield. A 512-channel analyser coupled with a 3 × 3 in. NaI(Tl) crystal was used to demonstrate the radiochemical purity.

Target preparation

Enriched ^{114}Cd in oxide form obtained from Oak Ridge National Lab. (U.S.A.) was used for the irradiation; it had the following specification.

Isotope	Atomic %
^{106}Cd	<0·01
^{108}Cd	<0·01
^{110}Cd	0·07
^{111}Cd	0·09
^{112}Cd	0·26 ± 0·02
^{113}Cd	0·33 ± 0·02
^{114}Cd	99·09 ± 0·05
^{116}Cd	0·07 ± 0·02

A spectrographic analysis was also provided and showed that the content of other elements was

Al, Cr, Co, Ga, In, Ni, Pt, Sb, Ta, W, Zr, Li < 0·05%;
Ag, B, Ba, Ca, K, Mg, Sr, Ti < 0·01%;
Cu, Na, Si 0·1%; Bi, Fe, Mn, Mo, Pb, Rb, Sn, V < 0·02%;
Zn, Th < 0·2%; Be < 0·001%.

Enriched ^{114}CdO (1·0 mg) was enclosed in a quartz ampoule and irradiated for 2 hr with a pile factor of 1500 for thermal neutrons. The nuclides 9·2-mCi ^{115}Cd (2·3 day) and 0·08-mC i^{115m}Cd (45 day) were calculated to be produced during the irradiation.

Determination of distribution ratio

To 2 ml of a buffer solution, tracer solution (0·1–0·2 ml, activity 5000–10000 cpm, containing 10–20 μg of the ion concerned) was added, 2 ml of 1% solution of PMCyP in IBMK were mixed into it, and the whole was shaken for 1 min. The phases were centrifuged, separated and counted. The activities of the organic phase were measured before and after equilibration by counting the characteristic radiations. The activities in the aqueous phase were also measured for material balance. The distribution ratio (*D*) was calculated as the ratio between the activities in the organic phase and the aqueous phase.

Separation of ^{115m}In

The irradiated quartz ampoule was broken carefully in a 50-ml conical flask and the target was dissolved in 2 ml of 1*M* hydrochloric acid (behind lead shielding) and heated to dryness. The residue was dissolved in 10 ml of aqueous solution buffered at pH 2·8 (26·42 ml 0·1*M* hydrochloric acid + 50 ml of 0·1*M* potassium hydrogen phthalate and diluted to 100 ml). The solution was transferred to another conical flask. The quartz ampoule was rinsed with 5 ml of buffer solution to free it from adhering active cadmium. The 15 ml of aqueous solution were preserved as a "cow" from which ^{115m}In was milked every day for a week. This was done by mixing 15 ml of 1% solution of PMCyP in IBMK with it, agitating the mixture with a magnetic stirrer for 1 min, and removing the organic

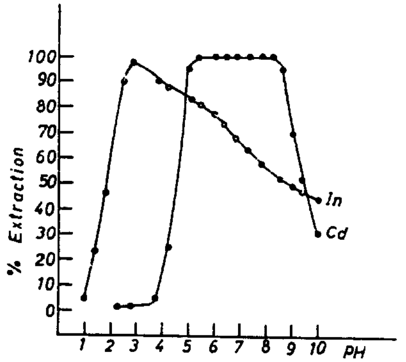


FIG. 1.—Effect of pH on the extraction of Cd and In with a 1% solution of PMCyP in IBMK.

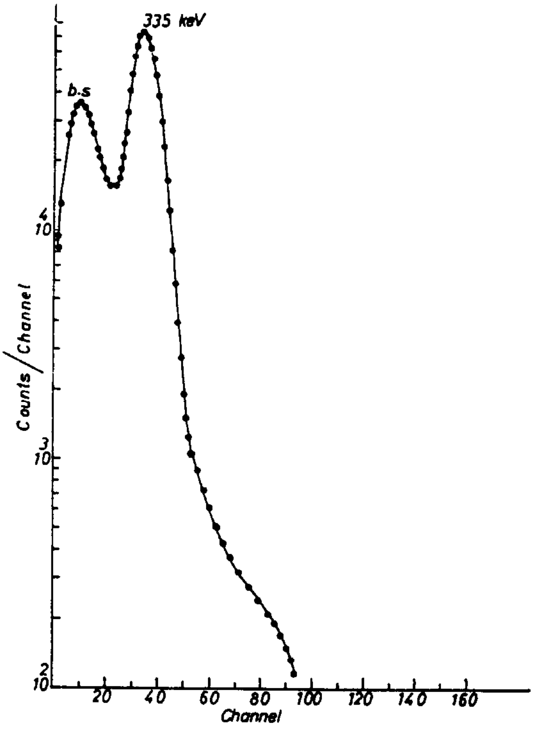


FIG. 2.—Gamma spectrum of ^{115m}In separated from irradiated cadmium. b.s. = back-scattering.

layer by pipette, leaving the aqueous layer for further growth of ^{115m}In. From the organic phase, ^{115m}In was stripped with 5 ml of 1*M* hydrochloric acid. The extraction cycle was repeated to obtain a good decontamination factor from cadmium. The final solution of ^{115m}In Cl_3 was obtained in 0·1*M* hydrochloric acid.

RESULTS AND DISCUSSION

The results reported are the mean of three runs. The extraction curves for cadmium and indium in Fig. 1 show that the extraction is pH dependent, cadmium being quantitatively extracted at pH 5·0–8·2 with negligible extraction below pH 3·0, and indium shows maximum extraction (98·5%) at pH 2·8. Extraction at controlled pH makes possible the separation of these two elements from each other. In the procedure used, the extraction at pH 2·8 carried 0·1% of cadmium activity along with the indium. The contamination by cadmium was further lowered by repeating the extraction cycle. The radiochemical procedure was tested by separating the indium activity from a synthetic mixture containing 20 μCi of ^{114m}In and 20 μCi of ^{109}Cd. The gamma spectrum of ^{115m}In separated from irradiated ^{114}Cd is reproduced in Fig. 2, and the main nuclear parameters of ^{115m}In and ^{115}Cd are given in Table I. No interference from cadmium activities was detected. Only one intense peak at ~335 keV was obtained and this was compared with a standard. A decontamination factor of 1 × 10^5 with a yield of 85–90% was obtained. The separation took less than 1 hr.

TABLE I.—MAIN NUCLEAR PARAMETERS OF ^{115m}In and ^{115}Cd

	Half-life, *hr*	E_β, *keV*	E_γ, *keV*
^{115m}In	4·5	840 (5%)	335 (95%)
^{115}Cd	53	590, 630 860, 1120	33, 230, 260 263, 493, 523

Acknowledgement—The author is thankful to B. Skytte Jensen for his help in the preparation of the reagent and for valuable discussions and to K. Heydorn, B. Kruse and U. Jacobsen for providing all the facilities. The fellowship awarded by D.A.E.C. under the bilateral agreement with P.A.E.C. is gratefully acknowledged. The work was carried out at the Isotopic Division, A.E.K. Risö, Roskilde, Denmark.

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Summary—A method is presented for the routine milking of the 4½-hr half-life nuclide ^{115m}In from its 2·3 day half-life parent ^{115}Cd. The method utilizes the extraction of In and Cd from aqueous solution at various pH values, 1-phenyl-3-methyl-4-caproylpyrazolone-5 in isobutyl methyl ketone being used as extracting agent. A good decontamination factor was obtained and the yield of ^{115m}In from residual cadmium activity was 85–90%.

Résumé—On présente une méthode pour la séparation de routine du nucléide ^{115m}In de demi-vie 4,5 h de son parent ^{115}Cd de demi-vie 2,3 h. La méthode utilise l'extraction de In et Cd d'une solution aqueuse à diverses valeurs du pH, la 1-phényl 3-méthyl 4-capryl pyrazolone-5 en isobutylméthylcétone étant employée comme agent d'extraction. On a obtenu un bon facteur de décontamination et le rendement de ^{115m}In à partir de l'activité résiduelle du cadmium a été de 85–90%.

Zusammenfassung—Eine Vorschrift zur routinemäßigen Abtrennung des Nuklids ^{115m}In mit 4,5 Stunden Halbwertszeit von seinem Mutternuklid ^{115}Cd mit 2,3 Tagen Halbwertszeit wird mitgeteilt. Die Methode verwendet die Extraktion von In und Cd aus wäßriger Lösung bei verschiedenen pH-Werten mit 1-Phenyl-3-methyl-4-caprylpyrazolon-5 in Methylisobutylketon als Extraktionsmittel. Es wurde ein guter Trennfaktor erhalten; die Ausbeute von ^{115m}In aus der restlichen Cadmiumaktivität betrug 85–90%.

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Precipitation of beryllium in presence of succinate by the urea hydrolysis technique

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In a previous communication[1] we reported our observations regarding the precipitation of beryllium in the presence of sulphate by the urea hydrolysis technique. We found subsequently that, as in the case of aluminium,[2] beryllium can be precipitated as a dense and easily filterable precipitate in the presence of phthalate and succinate. One obvious advantage of these latter ions is their easy removal from the precipitate. Also, the precipitates are denser than the basic sulphate. A detailed study of the precipitation of beryllium in presence of these ions was therefore made. Precipitation in presence of phthalate[3] takes place at a higher pH than that in presence of succinate and has no special advantages. The precipitates behave similarly to the basic sulphate.

EXPERIMENTAL

Reagents and apparatus

Beryllium nitrate solution. Standardized gravimetrically by the ammonia precipitation method.

Potassium succinate solution, 10% *w/v.*

All solutions were filtered to remove any suspended impurities, and were made from analytical grade reagents.

The apparatus was that used previously.[1]

Procedure

The solution containing 7–40 mg of beryllium, 1 g of potassium succinate and 4–6 g of urea is diluted to 250 ml and gently boiled on a hot-plate for 1 hr, the volume being kept constant by addition of distilled water from time to time. The precipitate is allowed to settle and filtered off on a Whatman No. 41 paper with a little pulp at the apex. The precipitate sticking to the walls is removed with a policeman. Finally, the beaker and stirring rod are treated with hot dilute hydrochloric acid and any beryllium removed is precipitated with ammonia and transferred to the filter. The precipitate is washed with 2% ammonium nitrate solution and ignited to the oxide at 1000° for 1½ hr. Typical results are given in Table I.

RESULTS AND DISCUSSION

Beryllium can be estimated quantitatively in the range 7–40 mg (Table I). The precipitation under the conditions described starts at a pH of 5·4–5·6 and is complete at a pH of about 8·3 (Tables II and III). If ammonium salts are present, the results tend to be low. This is attributed to the buffering action of the succinate–ammonium salt system which prevents the attainment of the required pH. When potassium succinate was replaced by succinic acid, no precipitation occurred even in the absence of ammonium salts, under the conditions given.

As in the case of the basic sulphate, the co-precipitation of calcium, magnesium and manganese is reduced to about a third of that in the ammonia precipitation. The determination of 25 mg of beryllium is quantitative in the presence of 800 mg of calcium, 300 mg of magnesium and 40 mg of manganese.

Table I.—Determination of beryllium as oxide

BeO taken, *mg*	BeO found, *mg*	pH of filtrate
25·8	25·9	8·3
64·6	64·6	8·3
90·5	90·6	8·4
90·5	90·3	8·3
120·0	119·7	8·3

Table II.—Change of pH with time

Time of boiling, *min*	pH
0	5·1
5	5·4–5·6 (opalescence appears)
20	6·9
40	8·1
60	8·3
90	8·4
120	8·6

TABLE III.—RECOVERY OF BERYLLIUM AS A FUNCTION OF pH

pH	Recovery, %
6·4	90·1
6·5	92·6
6·7	96·0
6·9	96·9
7·0	97·5
8·1	98·3
8·3	99·5
8·4	99·9

Thermogravimetric experiments on the vacuum-dried precipitate showed that it behaves similarly to the basic sulphate. The precipitate incorporates measurable amounts of succinate probably as a basic salt, but the succinate can be easily removed by ignition below 600°. There are three prominent regions of weight loss in the differential curve. The first peak at about 110° represents loss of superficial water from the precipitate. The second peak at about 260°, which is also observed in the case of the basic sulphate,[1] represents the pyrolysis of $Be(OH)_2$. The third peak at 430° (~750° in the case of basic sulphate,[1] 550° in the case of phthalate) represents the conversion into the oxide. The weight loss is complete at 530°, a temperature far less than that needed for the basic sulphate (~950°) and somewhat less than for phthalate (~600°).

The infrared absorption spectrum of the vacuum-dried precipitate has broad peaks at 3600, 2700 and 2300 cm^{-1}, medium broad peaks at 1580, 1300 and 1020 cm^{-1} and a sharp peak at 3450 cm^{-1}. The peaks at 1580 and 1300 cm^{-1} are attributed to the antisymmetric and symmetric vibrations of the carboxylate group,[8] and those at 3600 and 3450 cm^{-1} to the O—H stretching vibrations of beryllium hydroxide and free water respectively. The peak at 1020 cm^{-1} is assigned to the O—H bending vibration of the beryllium hydroxide.[1] The infrared spectrum of the precipitate heated for 2 hr at 400° shows the absence of peaks at 3600, 3450 and 1020 cm^{-1}, but the peaks at 1580 and 1300 cm^{-1} remain uneffected. This is to be expected as the latter two peaks represent the ionized COO^- group of the succinate and at this temperature the succinate is not eliminated completely from the precipitate (*cf.* the thermogravimetric results). This indicates that the succinate is bound strongly, probably as a basic salt. X-ray examination showed that the precipitate is amorphous.

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Summary—Beryllium can be precipitated as a dense and easily filterable precipitate in presence of succinate by the urea hydrolysis technique. Calcium, magnesium and manganese do not interfere to the extent that they do in the ammonia precipitation. One advantage over the basic sulphate method is that the oxide is obtained at a considerably lower temperature. However, when ammonia salts are present, the basic sulphate method is to be preferred.

Zusammenfassung—Beryllium kann in Gegenwart von Succinat mit der Harnstoffhydrolysenmethode als dichter und leicht filtrierbarer Niederschlag gefällt werden. Calcium, Magnesium and Mangan stören nicht im selben Maße wie bei der Ammoniakfällung. Ein Vorteil gegenüber der basischen Sulfatmethode ist der, daß das Oxid bei beträchtlich niedrigerer Temperatur erhalten wird. In Anwesenheit von Ammonsalzen ist jedoch die basische Sulfatmethode vorzuziehnen.

Résumé—On peut précipiter le béryllium sous forme de précipité dense et aisément filtrable en présence de succinate par la technique d'hydrolyse de l'urée. Le calcium, le magnésium et le manganèse ne

gênent pas autant qu'ils le font dans la précipitation à l'ammoniaque. Un avantage sur la méthode au sulfate basique est dans le fait que l'oxyde est obtenu à une température considérablement plus basse. Toutefois, en présence de sels d'ammonium, la méthode au sulfate basique doit être préférée.

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A new oxidimetric reagent—potassium dichromate in a strong phosphoric acid medium—VIII

Potentiometric titration of molybdenum(VI) and vanadium(V)

(*Received* 22 *December* 1966. *Revised* 28 *June* 1967. *Accepted* 21 *July* 1967)

IT has been reported that iron(II) can reduce molybdenum(VI) in 7–12*M* phosphoric acid.[1] The reaction is complete within a minute when a twofold excess of iron(II) is added, and a solution results which contains molybdenum(V), iron(II) and iron(III). We have found that a differential potentiometric titration of the excess of iron(II) and then of the molybdenum(V) is possible, dichromate being used as oxidant in solutions containing phosphoric acid at concentrations greater than 11·5*M*. In 12*M* acid, two distinct potential breaks are observed: the first corresponds to the completion of the oxidation of iron(II), and the second to that of the oxidation of molybdenum(V). The procedure provides an accurate and elegant, though slow, method for the determination of molybdenum(VI).

EXPERIMENTAL

Reagents

Molybdenum(VI) solution, 0·1*M*, was prepared from ammonium molybdate (B.D.H., AnalaR) and standardized.[2] Potassium dichromate solution, 0·2*N* was prepared from the Merck *pro analysi* grade reagent. A vanadium(V) solution, 0·1*M* was also prepared and standardized.[3] All chemicals were analytical reagent grade.

The potentiometric apparatus has been described.[4]

Procedure

Add from 2 to 8 ml of molybdenum solution (about 0·1*M*) to 40–50 ml of syrupy phosphoric acid, followed by a sufficient excess of iron(II) solution to reduce the molybdenum. The potential of the bright platinum electrode should be about 150–180 mV *vs.* the S.C.E. Stir the mixture and titrate with 0·2*N* dichromate solution, noting the potential 1 min after each addition for most of the titration, and after 10 min near the first break. Near the second break a wait of 2–3 min is sufficient. The potential increase at the first break is 30–90 mV per 0·04 ml of titrant, and at the second 250–300 mV. The volume of titrant between the breaks corresponds to the amount of molybdenum. Some results are shown in Table I.

TABLE I.—TITRATION OF MOLYBDENUM(VI)

Molybdenum						
taken, *mg*	$29{\cdot}2_6$	$38{\cdot}7_7$	$48{\cdot}4_6$	$60{\cdot}0_8$	$69{\cdot}9_5$	$77{\cdot}5_3$
found, *mg*	29·4	39·0	48·5	59·9	69·9	77·2

gênent pas autant qu'ils le font dans la précipitation à l'ammoniaque. Un avantage sur la méthode au sulfate basique est dans le fait que l'oxyde est obtenu à une température considérablement plus basse. Toutefois, en présence de sels d'ammonium, la méthode au sulfate basique doit être préférée.

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found, *mg*	29·4	39·0	48·5	59·9	69·9	77·2

TABLE II.—TITRATION OF MOLYBDENUM AND VANADIUM TOGETHER

Molybdenum					
taken, *mg*	$29{\cdot}0_7$	$38{\cdot}7_7$	$48{\cdot}4_6$	$58{\cdot}1_5$	$77{\cdot}5_3$
found, *mg*	29·1	38·8	48·5	58·0	77·2
Vanadium					
taken, *mg*	$23{\cdot}2_1$	$15{\cdot}4_7$	$18{\cdot}0_6$	$12{\cdot}9_0$	$10{\cdot}3_1$
found, *mg*	23·3	15·5	18·0	12·9	10·4

Interferences

Aerial oxygen does not interfere, and neither do the following ions: Mn(II), Mn(VII), Cu(II), Ni(II), Co(II), Zn(II), Fe(III), Cr(III), Cr(VI), Ce(III), Ce(IV), Ti(IV), Th(IV), W(VI). Nitrate interferes, and chloride in concentrations above 0·01*M* causes a decreased potential break after the titration of the molybdenum. Uranium(VI) behaves as molybdenum and is titrated without a separate end-point. Vanadium(V) is reduced to vanadium(III) and then oxidized by dichromate to vanadium(IV) along with the molybdenum(V) being oxidized to molybdenum(VI). A further potentiometric break occurs as the vanadium (IV) is oxidized to vanadium(V), so that mixtures may be analysed and the molybdenum obtained by difference, Table II shows some results from titrations of mixtures.

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Summary—A new titrimetric method is described for the determination of molybdenum(VI) involving prior reduction to Mo(V) with an excess of Fe(II) in a concentrated phosphoric acid solution, followed by titration with dichromate. The titration can be done at room temperature and without protective atmosphere. Uranium interferes, but vanadium may be determined simultaneously.

Zusammenfassung—Eine neue titrimetrische Vorschrift zur Bestimmung von Molybdän(VI) wird beschrieben: es wird zuerst mit überschüssigem Eisen(II) in einer konzentrierten Phosphorsäurelösung zu Molybdän(V) reduziert und dann mit Dichromat titriert. Die Titration kann bei Zimmertemperatur und ohne Schutzgas stattfinden. Uran stört, Vanadium dagegen kann gleichzeitig bestimmt werden.

Résumé—On décrit une nouvelle méthode titrimétrique pour le dosage du molybdène(VI) comprenant une réduction préalable en Mo(V) avec un excès de Fe(II) dans une solution d'acide phosphorique concentré, suivie d'un titrage au bichromate. Le titrage peut être effectué à température ordinaire et sans atmosphère protectrice. L'uranium gêne, mais on peut déterminer simultanément le vanadium.

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Switching valves for use in multi-column gas chromatography

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AN ARRANGEMENT in which two columns operate in parallel with differing gas streams is frequently of utility in gas chromatography. We describe here two forms of switching valve, tested over a long period, one developed to produce a sharp step-front for frontal analysis, and the other, diversion of an analytical elution sample into either of a pair of columns which are operated with different carrier gases and/or possibly with different detectors. Although the valves have much in common in design, they are described separately for convenience.

Total stream-switching valve

The problems of producing step boundaries for frontal analysis are well known. Our studies lead us to believe that the approach whereby such boundaries are most readily obtained is the total switching of an established equilibrated stream from one column to another, as nearly as possible identical, column through which previously flowed an equilibrated stream of different composition. The flow pattern is illustrated in Fig. 1. Initially, stream α, of constant composition, flows into column A and is allowed to establish equilibrium; simultaneously, stream β enters column B and is also equilibrated. On switching, stream α enters column B and β enters column A. A step concentration front is thus introduced into each column.

The valve devised for this purpose is illustrated in Fig. 2 and consists of an adaptation of the stainless steel rotary valves, working on the sloping O-ring principle, employed by us in similar devices.[1,2,3] The key has five grooves, two at 45° and three perpendicular to the axis of the key, and each groove contains a rubber O-ring. The sloping rings act effectively as two on/off valves. With the key in the position shown in Fig. 2, gas stream α enters *via* port 1 and leaves *via* port 4 to column A; stream β meanwhile enters *via* port 2 and leaves for column B *via* port 3. The five ports shown are in the same plane through the axis of the key and so, on rotation of the latter through 180°, stream α is diverted to leave through port 3 for column B, while stream β is diverted to leave through port 4 for column A. Since the key can be rotated rapidly and dead spaces between key and barrel are extremely small ($<0{\cdot}15$ ml), the frontal boundaries established are very sharp. The procedure has the further advantage of allowing both streams to be accurately set up and monitored before switching.

Figure 3(i) shows a boundary produced by operating the valve, while Fig. 3(ii) shows the boundary obtained on subsequent rotation through a further 180°, the initial conditions being re-established. It is seen that an 80% step-change occurs within 2–3 sec, the normal response time of the katharometer and read-out system used. If both streams contain only permanent gases and no organic vapour, a 100% step-change is obtained within the same period of time.

Stream selector

In any analysis of a wide boiling range mixture it is commonly the case that early pairs present the greatest difficulty of separation. Particular difficulty is experienced when one or both members of such a pair ($X + Y$) are permanent gases since an enormous theoretical plate requirement may then ensue for what is otherwise a simple analysis. A simple device to eliminate this need for high column efficiency is to conduct separate analyses of the same sample with two columns, using one of the two components concerned (say X) as the carrier gas in one case, and a different gas Z in the other.

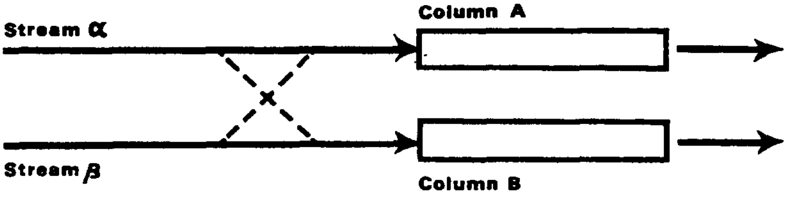

FIG. 1—Flow diagram for total stream-switching valve.

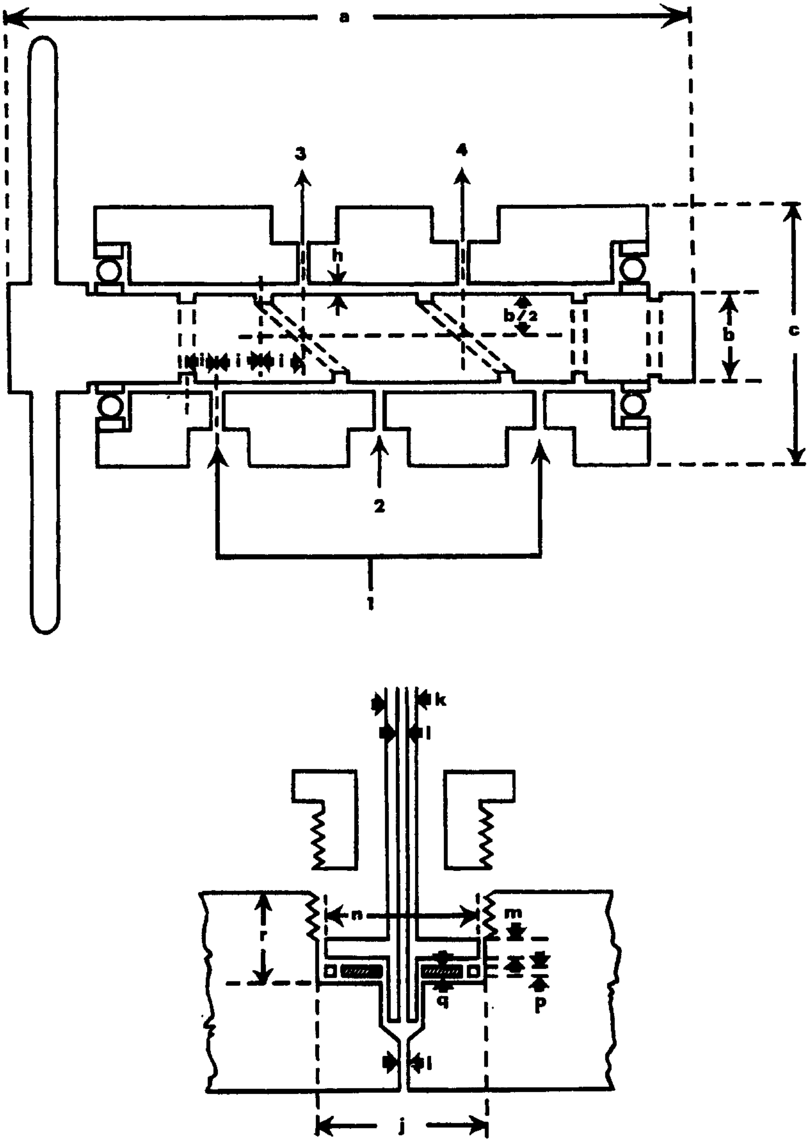

Fig. 2.—Diagram of total stream-switching valve and details of construction of a port.

a 5·06 in.
b 0·670 in.
c 1·93 in.
h 0·002 in.
i 1/4 in.
j 0·445 in.
k 0·12 in.
l 0·05 in.
m 0·08 in.
n 0·42 in.
p 0·04 in.
r 0·33 in.

Rubber rings in ports: $q = 0{\cdot}047$ in.

Sloping grooves: lead 1·085 Mc setting, depth 0·085 in., width 0·09375 in. O-rings to fit, 9/16-in. internal diameter × 0·103 in. section.

Perpendicular grooves: depth 0·080 in., width 0·118 in. O-rings to fit, 1/2-in. internal diameter × 0·103 in. section

Note: where 0·05-in. dia. holes break through into the bore, careful deburring is essential to avoid damage to the O-rings.

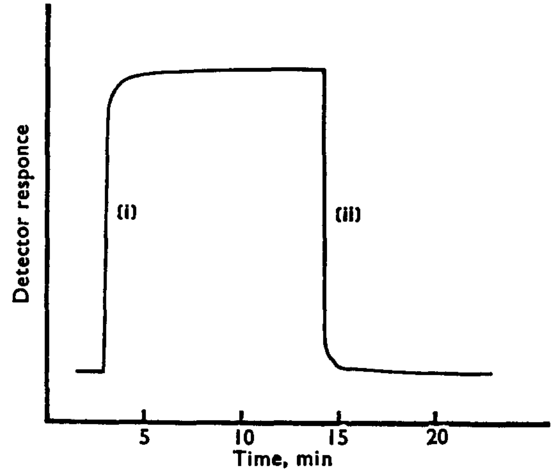

FIG. 3.—Step frontal boundaries observed with a katharometer situated between total stream-switching valve and one column. Valve operated so that (*i*) stream α is replaced by stream β, (*ii*) stream β is replaced by stream α.
Stream α: H_2 (73 cm Hg) + n-heptane (3 cm Hg)
Stream β: H_2 (76 cm Hg)
Flow-rate of each gas stream: 33 ml/min.

Quantitative analysis, based on previously determined calibration plots, can then be achieved by comparison of the two chromatograms obtained, since one yields a chromatographic peak of *Y* alone and the other, one of *X* + *Y*. If, of course, *Y* can also be used as carrier gas in place of *Z*, the second chromatogram will show *X* alone.

Figure 4 shows how this end is achieved by combining a slightly modified pair of the valves illustrated in Fig. 2 with a sampler, in this case one of the design described by Pratt and Purnell.[8] The two valves are mounted rigidly in tandem and each key carries a meshed gear wheel (1:1 gear ratio), the pair thus being capable of simultaneous rotation so that operation of the valve assembly is simplified. In the configuration shown in Fig. 4, the carrier stream *Z* travels *via* ports 1, 3, 3′ and 1′ to column *A* while carrier stream *X* goes *via* ports 2 and 4 to the sampler and thence to 4′, 2′ and column *B*. On rotation of both keys through 180°, stream *X* goes to column *B via* ports 2, 5, 5′ and 2′ while stream *Z* now travels *via* 1 and 4 to the sampler and then through 4′ and 1′ to column *A*.

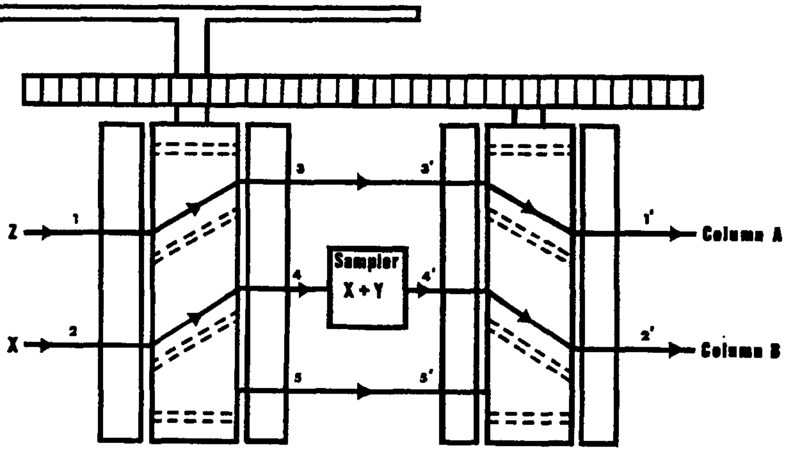

FIG. 4.—Flow diagram for stream selector valve.

The injections into the two columns may be made consecutively as quickly as the sampler can be evacuated and refilled with sample.

The lengths of connecting tubes are such that their volumes are made as small as possible, and approximately equal. It is seen that operation of the valve assembly changes the carrier gas flowing through the sampler without altering the flow-rate of either gas through its respective column. The only evidence seen on the chromatogram of the switching operation is the observation, after carrier X is switched into the sampler, of a small Z peak, or, after carrier Z is switched into the sampler, of a small X peak. The extra peaks represent residual gas swept out of the connections between ports 4 and 4′ on changing the carrier. Before analysis is attempted, it is necessary to allow this residual gas to be totally swept out, otherwise ambiguity can arise as to whether, say, the X peak comes from the residual gas or the injected sample containing X. In practice the delay involved rarely exceeds 2 min.

This valve has for some years been used continuously to expedite the rapid, repetitive analyses of hydrogen and monosilane mixtures.[4] The required column lengths were reduced by about a factor of ten which both speeded up analysis and increased markedly the peak height sensitivity of the thermal conductivity detector employed.

Details of construction

These are shown in Fig. 2. The key is mounted in ball-races at each end of the barrel. Since lubricating grease cannot be used where it will absorb the sample, silicone rubber is preferred to neoprene for the O-ring material because of its better self-lubricating properties. Various types of gas-tight sealing have been tried in the valve ports and that found to be most effective is shown in Fig. 2. A brass ring of 0·42 in diameter and 0·08 in. thickness is hard-soldered into the stainless steel connecting tubing about 0·2 in. from the end of the latter. A neoprene or silicone rubber disc, 0·047 in. thick, is fitted on to the end of the tube between the brass disc and the seat of the port and is prevented from splaying outward by a brass ring, 0·04 in. deep and 0·04 in. thick. The connector fits snugly into the valve port and is held firmly in position by a 0·5-in. diameter brass union.

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Summary—Two switching valves for use in multi-column and frontal gas chromatography are described. Constructional and operational details are given and examples of use are quoted.

Zusammenfassung—Zwei Umschaltventile zur Verwendung bei der Frontal-Gaschromatographie und mit mehreren Säulen werden beschrieben. Einzelheiten von Konstruktion und Bedienung sowie Anwendungsbeispiele werden angegeben.

Résumé—On décrit deux valves de mise en circuit pour emploi en chromatographie en phase vapeur à multi-colonnes et frontale. On donne les détails de construction et de manipulation et mentionne des exemples d'utilisation.

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Gravimetric determination of copper(II) with *p*-aminobenzoic acid

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FUNK and Ditt[1] were first to use the sodium salt of *o*-aminobenzoic acid (anthranilic acid) for the gravimetric determination of zinc, cadmium, cobalt(II), nickel and copper(II). The reagent was later used for the determination of manganese(II), lead and mercury(II).[2–4]

The advantage of the reagent is that the precipitates are nearly insoluble in water and alcohol and are not hygroscopic, and *o*-aminobenzoic acid liberated from the precipitates by means of acid can be determined by bromate–bromide titration.

Metal anthranilate precipitates are very stable. Their thermal behaviour has been investigated by Liptay[5] and by Erdey and Liptay[6] by the derivatographic method,[7] and in continuation of these studies the thermal decomposition of various metal salts of *m*- and *p*-aminobenzoic acids.[8] It has been found that copper(II) is quantitatively precipitated by *p*-aminobenzoic acid, and can be separated from zinc. We wished to use this phenomenon for analytical purposes.

The precipitate has the composition $Cu(C_7H_6O_2N)_2$, and on heating starts to decompose at about the same temperature as copper(II) *m*-aminobenzoate, 250°, which is 20° lower than the decomposition temperature of the rather stable *o*-aminobenzoate. The *p*-aminobenzoate is completely transformed into copper(II) oxide at 400° whereas this occurs with the *m*-aminobenzoate at a much higher temperature, 550–600°. This might be taken as indicating that the *para* compound is less stable than the *ortho* and *meta* compounds. The infrared spectrum of the precipitate, however, shows that the compound is a complex (judging by the position of the NH bands).

If the precipitation is effected from cool solution and the precipitate filtered off soon after precipitation and then dried, the precipitate weights are lower than the theoretical. If the solution and precipitate are allowed to stand for some hours, the precipitate will be crystalline and dark green, but its weight (after filtration and drying) will be higher than the theoretical. The composition of the precipitate is not stoichiometric in either case. If the precipitation is effected from hot solution, the precipitate contains no water of crystallization, and its composition is stoichiometric.

A 50–100% excess of reagent should be used in order to decrease the solubility of the precipitate.

Since *p*-aminobenzoic acid is highly soluble in alcohol, its solution in methanol or ethanol has also been tried as precipitant. However, if the solution is concentrated, the reagent is precipitated as well as the copper salt, and the weight of precipitate is too high. The same phenomenon was observed when an alcoholic solution of the reagent was used as wash-liquid.

The pH of precipitation is important. The weight of precipitate obtained from a slightly acidic unbuffered solution was 10–20% low and at pH <3 no precipitate was formed. The precipitate obtained at about pH 6 was also less than expected, presumably because of simultaneous precipitation of copper(II) hydroxide.

The optimum conditions for drying the precipitate were determined derivatographically. The precipitate is of constant weight up to 250°, then suddenly begins to decompose exothermally. At 440° conversion into copper(II) oxide is complete. The decomposition products reduce copper(II) oxide to a slight extent, but the copper(I) oxide is reoxidized in the presence of oxygen at higher temperatures, as soon as the reducing compounds have all been removed.

EXPERIMENTAL

Reagents

Copper sulphate solution, 0·06*M*. Standardized electrogravimetrically.

Buffer solution. Acetic acid–acetate, 0·2 *M*.

Precipitant solution. Make a saturated solution (~1·6% w/v) of *p*-aminobenzoic acid in 0·1*M* sodium hydroxide.

Procedure

Adjust the pH of the solution (containing 20–100 mg of copper) to 4–4·6 with about 20 ml of 0·2*M* acetic acid-acetate buffer in a beaker. Heat the solution to boiling, add to it 30 ml of *p*-aminobenzoic acid solution dropwise with constant stirring, and allow to stand on a steam-bath for 2–3 hr. Let the solution cool, and filter off the precipitate on a sintered glass crucible (porosity 4), wash it 4 or 5 times with distilled water, then dry it at 80–100° for 90 min. The solution and precipitate can be allowed to stand overnight instead of being heated on the steam-bath. The conversion factor is 0·1892.

RESULTS

Table I shows the difference between the values obtained by this method and by the electrogravimetric method. The standard deviation for 199·2 mg of precipitate was 0·58 mg (12 measurements).

TABLE I.—RECOVERY OF COPPER

Precipitate weight, *mg*	Copper		Difference, *mg*
	Found, *mg*	Taken, *mg*	
199·4	$37{\cdot}7_3$	37·80	$-0{\cdot}0_7$
199·1	$37{\cdot}6_7$		$-0{\cdot}1_3$
199·6	$37{\cdot}7_7$		$-0{\cdot}0_3$
198·2	$37{\cdot}5_0$		$-0{\cdot}3_0$
199·2	$37{\cdot}6_9$		$-0{\cdot}2_1$
199·8	$37{\cdot}8_1$		$+0{\cdot}0_1$
495·6	$93{\cdot}7_8$	94·50	$-0{\cdot}7_2$
507·2	$95{\cdot}9_7$		$+1{\cdot}4_7$
495·7	$93{\cdot}8_0$		$-0{\cdot}7_0$
498·7	$94{\cdot}3_6$		$-0{\cdot}1_4$
495·0	$93{\cdot}6_6$		$-0{\cdot}8_4$
499·4	$94{\cdot}5_0$		$0{\cdot}0_0$

Silver, mercury(II), lead, aluminium and iron(II) interfere by giving precipitates with the reagent. Bismuth, antimony(III) and tin(II) interfere by giving insoluble hydrolysis products.

TABLE II.—DETERMINATION OF COPPER IN PRESENCE OF EQUIMOLAR AMOUNTS OF ZINC

Precipitate weight, *mg*	Copper	
	Found, *mg*	Taken, *mg*
199·1	$37{\cdot}6_7$	
199·4	$37{\cdot}7_3$	37·80
198·9	$37{\cdot}6_3$	
498·0	$94{\cdot}2_8$	
498·6	$94{\cdot}3_3$	94·50
494·9	$94{\cdot}0_1$	

Though zinc, nickel, cadmium and cobalt(II) give insoluble *o*-aminobenzoates, they do not give *p*-aminobenzoates under the conditions prescribed, and do not interfere even if present in 10:1 molar ratio to the copper present. Table II shows typical results for copper in the presence of equimolar amounts of zinc.

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Summary—A method has been developed for the gravimetric determination of 20–100 mg of copper(II) with *p*-aminobenzoic acid. Ag, Hg(II), Pb, Al, Fe(II), Bi, Sb(III) and Sn(II) interfere, but Zn, Co(II), Ni and Cd do not. The precipitate can be weighed after drying at 80–100°, or can be ignited to copper(II) oxide at temperatures above 400°, and weighed in this form.

Zusammenfassung—Eine Methode zur gravimetrischen Bestimmung von 20–100 mg Kupfer(II) mit p-Aminobenzoesäure wurde entwickelt. Ag, Hg(II), Pb, Al, Fe(II), Bi, Sb(III) und Sn(II) stören, Zn, Co(II), Ni und Cd hingegen nicht. Der Niederschlag kann nach Trocknen bei 80–100° ausgewogen oder bei Temperaturen über 400° zu Kupfer(II)-oxid verglüht und in dieser Form ausgewogen werden.

Résumé—On a élaboré une méthode pour le dosage gravimétrique de 20–100 mg de cuivre (II) au moyen d'acide *p*-aminobenzoïque, Ag, Hg(II), Pb, Al, Fe(II), Bi, Sb(III) et Sn(II) interfèrent, mais Zn, Co(II), Ni et Cd ne gênent pas. On peut peser le précipité après séchage à 80–100°, ou le calciner en oxyde de cuivre (II) à des températures supérieures à 400° et le peser sous cette forme.

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LETTERS TO THE EDITOR

Note on the various methods of ion separation by electrolytic migration in a counter-current system

SIR,

Recently three papers were published[1] on the application of counter-current ionic migration to the separation of mixed-ligand complex ions and of ions that are chemically very similar. As separating column a capillary tube was used, connecting two compartments flushed with pure components of extremely different ionic mobilities. During electrolysis a sharp boundary would be stabilized between the two components, its location in the column depending only on the ratio of electric current to velocity of the counter-current flow.[2] An ion mixture to be separated, with ionic mobilities lying between those of the above-mentioned pure components, will "push" itself in this separating column between the end compartments; at steady state all the ionic compartments will "line up" in the sequence of their mobilities with a certain degree of overlapping.[3]

These experiments are very useful as they show a further application, not yet exploited, of counter-current ionic migration to chemical problems, but as it is claimed that a "new principle of counter-current ionophoresis" is demonstrated, a short review of the development of counter-current electromigration methods seems to be desirable.

Brewer and co-workers[4] as well as Martin *et al.*[5] deserve to be named here as the first investigators to apply the counter-current principle to ion migration in solution. Independently they found ways to test this new method by application to the enrichment of isotopes. They could make use of the advantage of having two opposed particle flows within one phase—electrical migration in one direction and transport by aqueous flow in the other—which led to a stationary separation profile of the components.

The efficiency of the process depends strongly on the extent to which "equilibrium" is established between the two particle flows. Besides this obvious difficulty, flowing liquids do not allow identical conditions over a given cross-section of the column, owing to the parabolic distribution of the flow velocities. Therefore the skilful design of a separating column is of extreme importance. From 1950 Clusius and co-workers[6] continued the experiments of Brewer, and divided the column into several compartments, which allowed a well-defined liquid flow even at rather large cross-sections.

All the three groups cited ran the counter-current process by some sort of manual or automatic regulation of the "equilibrium" between the electrical and aqueous flow transport of ions. Because of the extreme precision desired, the process became rather uneconomic and unsatisfactory.

Wagener[7,8] overcame this difficulty by simply letting the steady state build up by itself within given working conditions. The idea of this "self-stabilization" makes use of the simple fact that the local electric field strength in the column—which is determining the "counter-current equilibrium"—is only a function of the local concentration and the type of ions at a given electric current. This approaches ideal counter-current conditions, for the process follows any accidental fluctuations of the experimental environment by itself and needs no external regulation at all. The conditions for such a "self-stabilizing counter-current electrolysis" may be chosen within a wide range of limits, such as concentration of ions, composition of the electrolyte, acidity, temperature, *etc.*

Research along this line since 1960 has been directed towards the development of this method and the associated equipment.[9–15] Various applications have been published as well as a complete theoretical treatment of the process. The boundary conditions (for columns with and without end compartments, for closed and open separation, *etc.*), the dependence of the stationary ion concentration on the working conditions, the electric field curve of ions with large and small differences in mobility, the equilibrium time, the dependence of the separating factor on the isotope effect are taken into account in detail as well as the experimental consequences of these considerations. In recent papers the efficiency of bigger and improved electrolytic troughs of up to 1 mole capacity was studied.[13,14]

The well-known principle of counter-current electromigration opens a wide field of different applications. The new application to the separation of chemically similar complex ions, as described by Preetz,[1] provides a very helpful tool for analytical chemists. It should be pointed out, however, that the theoretical treatment of the process has been described elsewhere.

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Bemerkungen zum Verfahren der Gegenstromionophorese

In einer kürzlich erschienenen Notiz[1] wird ein geschichtlicher Abriß über die Methoden der Ionentrennung durch elektrolytische Wanderung in einer Gegenstromlösung gegeben. Dieser Aufsatz zeigt wie auch die Darstellung in unserer ersten Mitteilung,[2] daß die Ergebnisse zahlreicher Autoren zu dem jetzigen Stand der Wissenschaft auf diesem Gebiet beigetragen haben.

Ziel unserer Arbeiten ist es, das Gegenstromprinzip auf zweidimensionale kontinuierliche Trennungen, speziell zur präparativen Darstellung chemisch sehr ähnlicher Gemischtligandkomplexionen,[3] anzuwenden. Wie eine vierte,[4] in der genannten Notiz[1] nicht angeführte Arbeit zeigt, ist dies durch Weiterentwicklung einer seit langem bewährten Apparatur zur trägerfreien Durchflußionophorese[3,5] auch weitgehend gelungen. In den ersten drei Veröffentlichungen[2,6,7] wurden dafür die theoretischen und experimentellen Voraussetzungen mitgeteilt.

Unter Verwendung der Erkenntnisse aus Untersuchungen zur Methode der wandernden Grenzschicht[8] wählten wir eine Versuchsanordnung, die im Trennbereich der von Taylor und Dibeler[9] beschriebenen entspricht. Durch die Abtrennung der Elektrodentröge von dem eigentlichen Trennsystem mit Hilfe von Diaphragmen, die jede Konvektion verhindern, erübrigt sich bei uns die kontrollierte Spülung der begrenzenden Endzonen mit Lösungen bestimmter Konzentration. Die Elektrodenlösungen wählt man möglichst konzentriert, um sie nur gelegentlich erneuern zu müssen. Die Anodenlösung muß stets basisch, die Kathodenlösung sauer reagieren, damit die entstehenden H^+- bzw. OH^--Ionen, die den stationären Zustand stören können, sofort neutralisiert werden. Die Diaphragmen übernehmen erweiterte Elektrodenfunktionen, indem sie nicht wie diese meist nur als Quellen oder Senken für H^+- bzw. OH^--Ionen, sondern ganz allgemein als Quellen oder Sernken fü die beteiligten Kationen bzw. Anionen wirken (Preetz,[2] Abb. 1).

Für unsere Versuchsanordnung ließ sich das Funktionieren der Methode der wandernden Grenzschicht in ihrem klassischen Sinn[8] unter Gegenstrombedingungen und die automatische Steuerung des Trennvorgangs mit Hilfe einfacher theoretischer Überlegungen[2] und auch praktisch[6] uneingeschränkt nachweisen. Die herangezogenen Gesetzmäßigkeiten, nämlich diejenigen, die den Potentialverlauf an Grenzflächen und die Konzentrationsverteilung betreffen, sind durch Untersuchungen der Methode der wandernden Grenzschicht[8] bekannt und finden sich in Lehrbüchern.[10]

Bezüglich der sich selbststabilisierenden Gegenstromelektrolyse von Wagener[11] besteht neben anderen ein für unsere Zielsetzung wichtiger Unterschied. Während bei ersterem Verfahren über den gesamten Bereich der Trennsäule ein Grundelektrolyt (Säure bzw. Base) zugegen ist, grenzen bei der Gegenstromionophorese nach Erreichen stationärer Verhältnisse reine wäßrige Salzlösungen aneinander, die keine Fremdionen enthalten. Diese Tatsache ist wichtig für die präparative Darstellung aller Komplexionen, die leicht der Hydrolyse unterliegen.

Die Übertragung bekannter Prinzipien auf eine zweckmäßige Versuchsanordnung hat demnach zu einem neuen Verfahren geführt, dessen Bedeutung besonders im Bereich der Trennung und Reindarstellung empfindlicher Substanzen liegt.

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TALANTA REVIEW*

CHARACTERISTIC METAL–HALOGEN VIBRATIONAL FREQUENCIES OF COMPLEXES WITH BIVALENT METAL HALIDES

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Summary—Studies of the metal-halogen vibrational frequencies of complexes have been numerous and it is apparent that such frequencies are often characteristic of the structure and stoichiometry. The method, although generally applicable, is most valuable where neither ultraviolet spectra nor magnetic moments can be of assistance. The current literature is reviewed with the intention of facilitating the characterization of unknown materials derived from bivalent metal halides.

The advent of the commercially available far-infrared spectrometer operating in the region 400–20 cm^{-1} provides a valuable tool for the examination of many different types of system, including the study of weak interactions (*i.e.*, charge transfer, hydrogen bonding), rotational spectra and the vibrational spectra of heavier mass systems. In the latter category can be included the skeletal vibrations of ligand–metal–halide (L–M–X) complexes. Until recently, vibrational studies of such complexes were limited to an examination of the internal modes of the ligand appearing in the conventional region of the spectrum. This frequently gave information about the nature of bonding in the complex, as in the study of pyridine[1] and urea complexes.[2] However, direct examination of ligand–metal and metal–halogen vibrations is clearly a more satisfactory way of determining the nature of the bonding and the structure of complexes.

The majority of L–M–X complexes give rise to three types of characteristic vibration, namely, the internal modes of the ligand, and ligand–metal and metal–halogen vibrations. The degree of interaction of these modes will vary from compound to compound but separation into these groups is a reasonable generalization. In the majority of complexes which we have studied, the metal–halogen vibration gives rise to the most intense features of the spectrum, and these may also be identified as such by the wavelength shift that occurs when one halogen is substituted for another in complexes of similar structure. The number of metal–halogen peaks and their position in the spectrum will be dependent on a variety of factors such as structure, stoichiometry and oxidation state. It is the purpose of this review to correlate the information currently available about metal–halogen stretching frequencies with structure and stoichiometry when the metal is in the bivalent state.

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The literature of far-infrared spectroscopy is extensive, but a general review has been given by Wood,[3] and metal–halogen frequencies have been reviewed by Clark.[4]

INSTRUMENTAL METHODS

It is desirable that any spectrometer used for a study of metal–halogen frequencies should have a lower frequency limit not higher than 100 cm^{-1}. Conventional grating spectrometers within this specification include the Perkin–Elmer 301 and Beckman IR 11. Spectra may also be obtained in this region by interferometric techniques; interferometers include Grubb Parsons' "Iris", and Research and Industrial Instrument Company's Model 620 which must be used in conjunction with a digital computer or with the same company's Fourier Transform Computer, F.T.C. 100, in which case the combination functions as the equivalent of a double beam spectrometer. (The application of this rapidly expanding technique has been reviewed.[5])

SAMPLING

By use of polythene windows, examination of specimens in all three phases is possible. However, at longer wavelengths interference is a problem and all supporting windows in the radiation path must be wedged to minimize this effect.

The majority of samples run at the University of Strathclyde are in the form of dispersions in polythene. Originally it was suggested that disks in polythene could be prepared by dissolving the specimen in molten polythene.[6] In a modification of this method, 5–20 mg of sample are dispersed in 100 mg of precipitated polythene and then pressed in a wedged die. The resulting semi-transparent disk may then be mounted in the spectrometer in the same way as a KBr disk. This has the advantage over the nujol mull technique of being less likely to give interference patterns, and in many cases the disk may be stored for further study if desired. Unlike the halide disk method, there is no evidence so far of interaction of sample and polythene.

Because of the problems of solid state interactions it is desirable that spectra be obtained from solutions, and while there is no technical reason to prevent this, the majority of complexes of the type to be discussed are readily solvolysed and to date only a limited number of solution spectra have been reported.

The spectra illustrating this review were obtained, by use of an R.I.I.C. 620 and F.T.C. 100, from samples dispersed in polythene. Figures 1 and 2 have previously been shown by Clark and Williams[7,8] for the region up to 200 cm^{-1}.

IDENTIFICATION OF METAL–HALOGEN FREQUENCIES

Metal–halogen (M–X) peaks are most readily identifiable by the shift which occurs in their frequency when the spectra of chlorides, bromides and iodides of similar structures are compared., Moreover these shifts have been found with ratios M–Cl/M–Br $\sim$ 0·77 and M–Cl/M–I $\sim$ 0·65 in various compounds[7] and it seems likely that these ratios may be expected for most complexes of the types to be discussed, providing that the vibration observed is largely metal–halogen.

In a series of compounds with different metals the frequencies should also vary according to the Irving–Williams order, *i.e.*, $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. However, it is very unusual for copper complexes to have similar structures to those of other first row transition elements and almost always copper must be treated as a special case. A change from first to second to third transition series will also be accompanied by a shift of frequency, Ni > Pd > Pt or Zn > Cd > Hg. In this case relatively few series of complexes of similar structure are known and the situation is rendered more complex by the change in nature of bonding which occurs.

The number of M-X frequencies to be expected for a complex of any given symmetry may be calculated.[9] However, because of degeneracy or solid state interactions either more or less than this number may be observed in practice. Very frequently the expected number of bands is observed, particularly for M-X stretching frequencies.

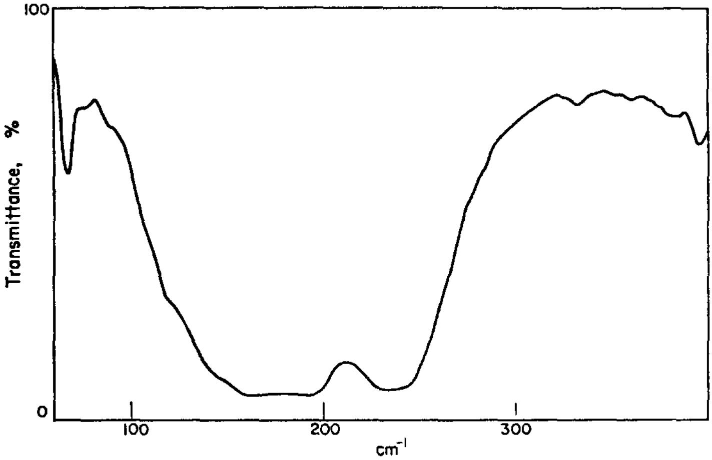


FIG. 1.—α-$(C_5H_5N)_2CoCl_2$ (violet octahedral dipyridine cobalt dichloride).

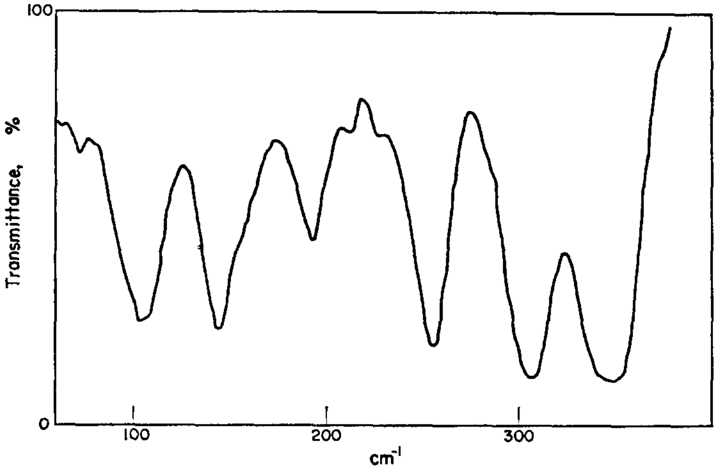


FIG. 2.—β-$(C_5H_5N)_2CoCl_2$ (blue tetrahedral dipyridine cobalt dichloride).

Table I collates the number of frequencies observed in practice and will be discussed in detail for individual structures.

Tetrahalometallate(II), MX_4^{2-}

This type of complex has been extensively studied,[10] usually in the form of a compound with an organic cation. A tetrahedral T_d ion should give rise to only one infrared-active stretch ν_3 and one infrared bend ν_4 if there is no interaction.

The data quoted (Table II) do not follow the Irving-Williams order; in particular the values for copper are discrepant and this is known to be due to the difference in structure, which is flattened from T_d to D_{2h}. The values for zinc, cadmium and mercury show the decrease in values expected on changing from first to second to third row. The two values of ν_3 for $ZnCl_4^{2-}$ illustrate the problems of choosing the maximum of what is often a broad band.

TABLE I.—M–X FREQUENCIES OBSERVED FOR VARIOUS STRUCTURES

	M–X stretch	M–X bend
Tetrahedral		
MX_4^{2-}	1	1
LMX_3^-	2	1
L_2MX_2	2	1
(1–1)MX_2*†	2	¶
Octahedral		
L_2MX_2*	1	¶
L_4MX_2	1	1
(1–1)$_2MX_2$†	1	¶
Planar		
MX_4^{2-}	1	3 or 4
LMX_3^-†	3	‡
(1–1–1)MX^+*†	1	¶
trans L_2MX_2	1	2
cis L_2MX_2	2	2

L = ligand; 1–1 = bidentate ligand; M = bivalent metal; X = halogen.

* Data available to 200 cm^{-1}.

† Limited data.

‡ δM–X mixed with δM–L.

¶ Not observed.

TABLE II.—TETRAHEDRAL MX_4^{2-}, M–X STRETCHING FREQUENCIES (ν_3, cm^{-1})

	Mn	Fe	Co	Ni	Cu	Zn	Cd	Hg	Ref.
$[Et_4N^+]_2[MCl_4^{2-}]$	284	286	297	289	267 248	277			10*
						271	260	228	10†
$[Et_4N^+]_2[MBr_4^{2-}]$	221	219	231	231 224	216 174	207			10*

* Sabatini and Sacconi

† Adams *et al.*

Recently Forster[11] has examined the spectra of $CoCl_4^{2-}$ and $CuCl_4^{2-}$ in solution and observed that for the former there is only one band at 296 cm^{-1} while for the latter there are two, at 278 and 237 cm^{-1}, indicating that $CuCl_4^{2-}$ remains distorted in solution.

The M–X bending frequencies (Sabatini and Sacconi[10]) are 123–145 cm^{-1} for MCl_4^{2-} and 85–92 cm^{-1} for MBr_4^{2-}.

Ligand metal trihalide, LMX_3^-

While complexes of the type L_2MX_2 and ions MX_4^{2-} are well known, far fewer compounds containing the ion LMX_3^- have been reported. Bradbury *et al.*[12] have examined the far infrared spectra of this type of compound, with Et_4N^+ as cation and L being either pyridine or triphenylphosphine (Table III). For the majority of these complexes the metal–halogen frequencies are observed to occur at positions intermediate between those of MX_4^{2-} and L_2MX_2. While theory predicts two metal–halogen stretching frequencies for a C_{3v} complex of this type, a greater number of bands is sometimes observed. This may be due either to solid state interaction or to the ligand reducing the symmetry of the complex. At lower frequencies one metal–halogen bending mode is observed, at about 130 and 100 cm^{-1} for the chloride and bromide respectively.

Diligand metal dihalide, L_2MX_2

The far-infrared spectra of a large number of complexes of this type have been recorded. On the basis of structural or spectroscopic evidence they may be divided into a number of types: tetrahedral or polymeric octahedral with bridging halogens, *cis* or *trans* square planar, and the special case of tetragonal copper complexes. Tetrahedral and polymeric octahedral are best dealt with together since frequently one ligand gives rise to compounds of either structure, depending on the metal under consideration. Thus, of compounds of the type dipyridine metal dichloride, the Fe(II), Mn(II) and Ni(II) complexes are polymeric octahedral, the Zn(II) complex is tetrahedral, and the Co(II) complex shows temperature-dependent structural isomerism. Examples of complexes of platinum and palladium existing as *cis* and *trans* planar isomers are very numerous, while a rather more limited number of *trans* planar nickel complexes have been reported. Copper complexes with Jahn-Teller induced tetragonally distorted structures occupy a position best regarded as intermediate between polymeric octahedral and *trans* square planar.

TABLE III.—TETRAHEDRAL LMX_3^-, M–X STRETCHING FREQUENCIES (cm^{-1})

	Co	Ni	Zn	Ref.
$[Et_4N^+][\phi_3PMCl_3^-]$	320, 282	308, 278	300, 276	12
$[Et_4N^+][\phi_3PMBr_3^-]$	252, 210	242, 212	228, 218 182	

It is in the differentiation of these types of complexes that study of metal–halogen vibrations seems most useful.

Tetrahedral and polymeric octahedral L_2MX_2

The differentiation of tetrahedral and polymeric octahedral isomers was one of earlier accomplishments of far-infared spectroscopy. Clark and Williams' studies[8] of pyridine complexes pointed out the ease with which the structural form could be identified, this being of particular value where ultraviolet–visible spectra or magnetic moments gave no indication of structure, as is the case for zinc and cadmium complexes. To date a number of studies of complexes of nitrogen donors with first row transition elements, zinc and cadmium have been reported[7,8,13] and a clear pattern has emerged in which the tetrahedral complex gives two peaks corresponding to metal–halogen stretching modes while in the octahedral form the metal–halogen peak is at a lower frequency. Much of the reported information has a lower limit of 200 cm^{-1} and this is only slightly lower than the highest metal–chlorine frequency for a polymeric chloride, and a detailed study of this type of complex below 200 cm^{-1} is therefore desirable. The spectra of the octahedral α forms of dipyridine cobalt dichloride and the β tetrahedral form are shown. The phase change is induced by heating the α form[8] to 120° or alternatively by incorporating about 1% of the tetrahedral zinc complex in the lattice to stabilize the β form.[14] Effectively the differentiation is between terminal M–X bonds and a non-linear M–X–M bond. As a consequence of the difference in bond character and stereochemistry there is a shift of some 80 cm^{-1} from the two metal–chlorine stretching frequencies observed for the tetrahedral complex to a single broad band at about 240 cm^{-1} for the polymeric

TABLE IV.—TETRAHEDRAL L_2MX_2, M–X SYMMETRIC AND ASYMMETRIC STRETCHING FREQUENCIES (cm^{-1})

L_2	$CoCl_2$	$CoBr_2$	$ZnCl_2$	$ZnBr_2$	Ref.
$(Pyridine)_2$	344, 304	274, 242	329, 296	254, 220	7, 13, 16
$(Triphenylphosphine)_2$	350, 316	272, 237	322, 299	235, 202	13, 19
(Triphenylphosphine oxide)$_2$	342, 317	249, 233			13
$(Thiourea)_2$	316, 294	235, 190	279, 252	200, 185	18

Frequencies for cobalt and zinc complexes usually represent the maximum and minimum frequencies respectively for a particular ligand.

Metal-iodide frequencies are usually outside the range reported but the data available follow the usual pattern.

	CoI_2	ZnI_2	
$(Thiourea)_2$	204, 184	176, 166	18

Second and third row elements usually form complexes of less regular structure; however, triphenylphosphine probably forms tetrahedral complexes with cadmium and mercury halides

	$CdCl_2$	$HgCl_2$	
$(Triphenylphosphine)_2$	268, 261	232, 221	19

At least one metal–halogen bending frequency is observed, usually 12, 19, 28 at about 100 cm^{-1}.

TABLE V.—POLYMERIC OCTAHEDRAL L_2MX_2, HIGHEST REPORTED X-SENSITIVE FREQUENCY (cm^{-1})

L_2	$MnCl_2$	$NiCl_2$	$CdCl_2$	Ref.
$(Pyridine)_2$	233	246	<200	7, 13
$(Quinoline)_2$	241	258	—	13
$(NH_3)_2$	240	—	215	20

No data available beyond 200 cm^{-1}.

TABLE VI.—TETRAHEDRAL (1–1)MX_2, M–X SYMMETRIC AND ASYMMETRIC STRETCHING FREQUENCIES (cm^{-1})

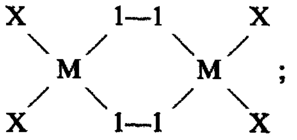
(1–1)	$CoCl_2$	$CoBr_2$	$ZnCl_2$	$ZnBr_2$	Ref.
Bipyridylamine	337, 318	256, 248	327, 305	233, 224	22
Ethylenediamine			315, 285		21
Dipyridyl			327, 322		20

chloride. Similar spectra have been reported for bipyridyl cobalt dichloride which exists in both octahedral and tetrahedral forms.[15]

Other ligands form an extensive series of tetrahedral complexes. Thus triphenylphosphine oxide,[16] triphenylarsine oxide,[17] thiourea,[18] and triphenylphosphine,[16,19] form complexes of formula L_2MX_2, and with the exception of the copper complexes where these are known, all appear to be tetrahedral. These series of complexes are all formed by relatively large ligands for which four-co-ordination will be sterically preferred.

A possible alternative structure is the dimeric form $[L_4M^{2+}][MX_4^{2-}]$. This type of structure, as will be discussed later, has been postulated in a number of instances but there have been no spectra reported where the structure is certain. In contrast to this the far-infrared spectrum of $(NH_3)_2ZnCl_2$ is exactly what would be expected for $[(NH_3)_4Zn^{2+}][ZnCl_4^{2-}]$ but an early X-ray structure has reported the compound to be of the tetrahedral L_2MX_2 type. The spectrum shows only one M–Cl stretch at 285 cm^{-1}, the position expected for $ZnCl_4^{2-}$.[20]

Complexes with a bidentate ligand [1–1)MX_2 could be either tetrahedral monomeric or dimeric



though the far-infrared method differentiates between terminal and non-terminal M–X groups it will not distinguish between the monomeric and the ligand-bridged dimeric forms, although of course the third alternative, bridging through halogens, will be clearly identifiable.[21]

Copper complexes, L_2CuX_2

Copper complexes of the type L_2CuX_2 or (1–1)CuX_2 usually give spectra very different from those of the other first row elements.[22] The structures, because of the Jahn-Teller effect, are normally distorted polymeric octahedral with four short and two long bonds and, for example, in dipyridine copper dichloride, chlorine atoms occupy a bridging position such that one Cu–Cl distance is shorter than the other. Thus the structure is related to that of other polymeric octahedral complexes but the M–X–M bonds are asymmetric.[23] This structure is one which may give metal–halogen stretching frequencies over a wide range, depending on bond lengths and strengths.[24] The two extremes of the structure may be represented by the case in which the long

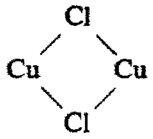
TABLE VII.—COPPER COMPLEXES L_2CuCl_2, FREQUENCIES IN cm^{-1}

L_2	$CuCl_2$	$CuBr_2$	Ref.
(Pyridine)$_2$	287, 229, 177, 90	256, 204, 132, 60	22*
(Quinoline)$_2$	330, 151, 84	266, 110, 52	22*
$(NH_3)_2$†	251	222, 205	15
(2, 3-Dimethylquinoxaline)	368	278	26

* Goldstein *et al.*

† Data to 200 cm^{-1} only.

Cu–X bonds are so extended as to make the complex effectively square planar, and the other where there are four identical Cu–X distances and the complex is effectively regular polymeric. Comparison of the data for square planar nickel[25] indicates that in the former case the Cu–Cl stretch could occur at as high as 400 cm^{-1} while for the latter the frequency would be expected at about 240 cm^{-1}. In practice the extremes of the range seem to be represented by 368 cm^{-1} for 2,3-dimethylquinoxaline copper dichloride[26] and 251 cm^{-1} for diamine copper dichloride.[15] For the majority of complexes within this range, only one band is assignable to a copper–chlorine stretching mode and this seems to be characteristic. This is similar to the one band observed for *trans* square planar complexes and undoubtedly the observed peak corresponds largely to the stretching mode of the short Cu–Cl bond. At lower frequencies two additional bands are observed and these must correspond to vibrations of the



chains.[22]

The assignment of spectra observed for a number of copper complexes of various stoichiometries has been discussed recently by Adams and Lock.[24] They point out that the dimeric pyridine-*N*-oxide copper dichloride has a structure with only terminal Cu–Cl bonds and this gives copper–chlorine stretches at 325(sh) and 315 cm^{-1}.

Five-co-ordinate, (1–1–1)MX_2

Few spectra of five co-ordinate complexes have been reported. Terpyridyl zinc and cadmium dichlorides each show two bands (288, 279 cm^{-1} for zinc; 269, 255 cm^{-1} for cadmium; data to 200 cm^{-1} only) which in the case of zinc are at slightly lower frequencies than would be expected for a tetrahedral complex.[27]

Octahedral complexes, L_4MX_2

Trans L_4MX_2 complexes would be expected to give only one stretching frequency and this was reported to occur at about 240 cm^{-1} for tetrapyridine cobalt and nickel dichlorides.[13] More recently the spectra of a wide range of tetrathiourea metal dihalides have been reported[18] and these give rise to two bands assignable to a metal–halogen stretch and a bend. On the basis of their spectra, the complexes appear to be

TABLE VIII.—OCTAHEDRAL COMPLEXES, FREQUENCIES (cm^{-1})

Type	L_4 or (1–1)$_2$	MX_2				Ref.
L_4MX_2	(Pyridine)$_4$	$NiCl_2$	244	$CoCl_2$	230*	7, 13
	(Thiourea)$_4$	$NiCl_2$	202, 144	$NiBr_2$	166, 110	18†
	(Benzimidazole)$_4$	$CuCl_2$	168‡	$CuBr_2$	130‡	28
(1–1)$_2MX_2$	(Biuret)$_2$	$NiCl_2$	200, 188‡	$NiBr_2$	140‡	28
	(Biuret)$_2$	$CuCl_2$	182‡	$CuBr_2$	120‡	

* Data to 200 cm^{-1} only.
† Adams and Cornell.
‡ M–X stretch only observed.

trans octahedral, as do the complexes tetrabenzimidazole copper dichloride and bromide;[28] for these, presumably because the halides occupy the long-bond positions, the frequencies are lower.

Octahedral complexes, $(1\text{–}1)_2MX_2$

The spectra of diarsine complexes of bivalent metals were examined by Lewis *et al.*[29] down to 200 cm^{-1} without any pattern for the metal–halogen vibrations emerging. However, a study of biuret complexes at longer wavelengths[28] indicates that metal–halogen frequencies appear in much the same region as for L_4MX_2 complexes. For these complexes some of the bands split but it is not known whether this indicates that the structures are *cis*.

Square planar, MX_4^{2-}

The spectra of this type of planar ion have been the subject of much study and considerable theoretical discussion.[30] While theory predicts four infrared-active modes, the predominant feature of the spectra is ν_6, an M–X stretching frequency. The remaining bands in the spectra have been assigned to bending and lattice vibrations. The data for ν_6 of $PdCl_4^{2-}$ (Perry *et al.*[30]) with various cations show decreasing frequency with increasing size of counter-ion, a feature observed for many spectra of ionic substances.[31]

TABLE IX.—SQUARE PLANAR MX_4^{2-}, FREQUENCIES (cm^{-1})

	ν_6, M–X stretch	M–X bends	Ref.
K_2PdCl_4	336	193, n.o. 110, 95	30*
K_2PdBr_4	260	140, 130, 100, 85	30*
K_2PtCl_4	325	193, 175, 106	30†
K_2PtBr_4	234	— — —	34†

ν_6 for $PdCl_4^{2-}$ salts: NH_4^+, 327; K^+, 336; Rb^+, 331; Cs^+, 328 30*
* Perry *et al.*
† Sabatini *et al.*
‡ Hendra and Sadasivan.
n.o. = not observed.

The single M–X stretching frequency observed for *trans* L_2MX_2 occurs at much the same wavelength as ν_6 for planar MX_4^{2-}, so it would not be possible to differentiate $[L_4M^{2+}][MX_4^{2-}]$ from trans L_2MX_2 in this instance.

Square planar, LMX_3^-

The far-infrared spectrum of Zeise's salt $K[C_2H_4PtCl_3]$ shows three strong bands (339, 331, 310 cm^{-1}) in the Pt–Cl stretching region as well as a number of bands at lower frequencies.[32] While the former appear to be purely Pt–Cl stretch, the latter must be regarded as bending modes of the entire skeleton.

Square planar cis *and* trans L_2MX_2

Formed by platinum and palladium and to a lesser extent by nickel, these complexes were amongst the earliest to be studied by far-infrared methods.[25,33]

Theory requires that the *trans* isomer should give only one metal–halogen stretch, while the *cis* isomer should give two. In most cases this is the pattern which is in practice observed and sufficient data have accumulated to define characteristic ranges, with the exception of Pd–Br frequencies.[33,34] More recently a number of spectra have been reported beyond 200 cm^{-1} (Durig *et al.*[30,35]) and both *cis* and *trans* complexes have two bending modes in this region.

TABLE X

Square planar cis L_2MX_2

Reported complexes have two M–X stretching frequencies (cm^{-1}) in the following ranges:

L_2PdCl_2	354–307, 346–287	L_2PdBr_2	insufficient data
L_2PtCl_2	360–302, 345–281	L_2PtBr_2	254–211, 226–193

In addition, two M–X bending frequencies have been reported* beyond 200 cm^{-1}:

(Pyridine)$_2$PtCl$_2$	163, 108	PtI$_2$	103, 88

Square planar trans L_2MX_2

Reported complexes have one M–X stretching frequency in the following ranges:

L_2PdCl_2	365–333	L_2PdBr_2	insufficient data		
L_2PtCl_2	343–326	L_2PtBr_2	259–227		
(Trimethyl phosphine)$_2$NiCl$_2$	403,	NiBr$_2$	340,	NiI$_2$	280†

Again two M–X bending frequencies have been reported:*

(Pyridine)$_2$PdCl$_2$	166, 122	PtCl$_2$	167, 125

* Durig *et al.*[35]
† Coates and Parkin.[25]

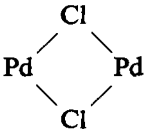
Generally the metal–halogen frequency for the *trans* complex occurs within a narrower range of values than do the two frequencies characteristic of the *cis* complex.[33]

Square planar [1–1–1MX]

The tridentate ligand diethylenetriamine forms a three-co-ordinate complex with palladium halides. The complexes show one Pd–X stretching frequency at 333 cm^{-1} for the chloride and 241 cm^{-1} for the bromide.[36]

Platinum(II) and palladium(II) bridging frequencies

Adams and Chandler[37] have reported data for a number of compounds containing halogen bridges and report two bands assignable to bridging frequencies in all the compounds studied. The higher frequency band is only a little lower than that observed for the *trans* monomeric complex, while the second is some 25–50 cm^{-1} lower. Lupin *et al.*[38] have reported data for compounds (allyl)$_2$Pd$_2$Cl$_2$ and these also show two bands assignable to the



bridge.

SOME RECENT APPLICATIONS OF FAR INFRARED SPECTROSCOPY

Identification of MX_4^{2-}

Clark and Williams[15] have observed the metal-chlorine stretching frequency of MCl_4^{2-} in the decomposition products $MCl_2(\text{bipyridyl})_{1\cdot33}$ derived from complexes $MCl_2(\text{bipyridyl})_3$ (where M = Co or Ni). Similarly, they identify the dihydrochloride of $CoCl_2$·bipyridyl as $[\text{bipyridyl-H}^+]_2[CoCl_4^{2-}]$ on the basis of bands at 306, 294, 282 cm^{-1}, which it is suggested are due to ν_3 of $CoCl_4^{2-}$ split by site symmetry effects.

Dimethyl sulphoxide adducts of formula $(DMSO)_3MCl_2$ (M = Mn, Co, Ni) have been known for some time.[39] On the basis of visible spectra they have been assigned formulae $[(DMSO)_6M^{2+}][MCl_4^{2-}]$ and the presence of MCl_4^{2-} has been confirmed by far-infrared studies.[40]

Adducts of alkyl and aryl halides with phosphine metal halide complexes

Bistriphenylphosphine metal dihalides $[(\phi_3P)_2MX_2]$ form adducts $(\phi_3P)_2MX_2$·1 or 2RX which from visible–near-infrared spectra and magnetic moments have been

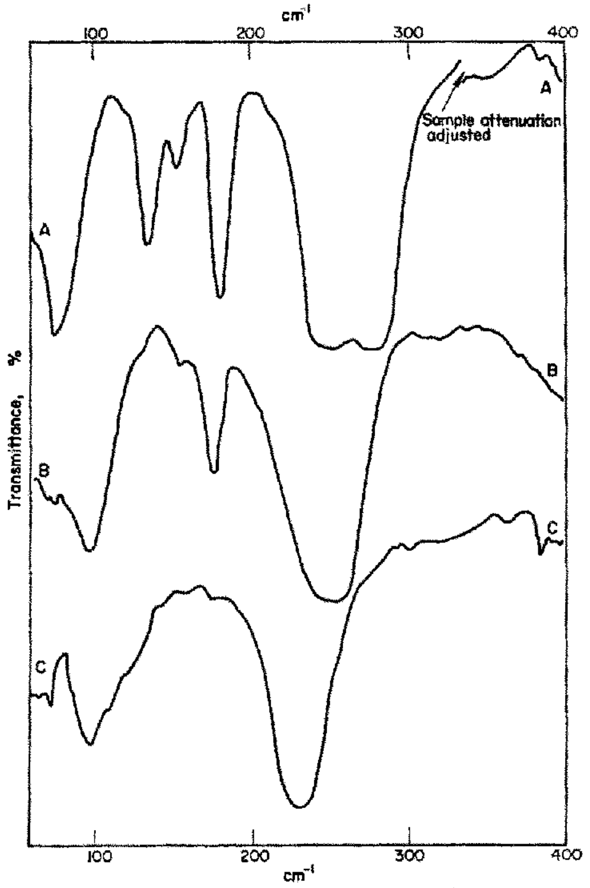


FIG. 3.—Adducts of dipyridine cobalt dibromide.
A—A Py_2CoBr_2.
B—B $[PyC_3H_7^+][PyCoBr_3^-](Py_2CoBr_2\cdot C_3H_7Br)$.
C—C $[PyC_3H_7^+]_2[CoBr_4^{2-}](Py_2CoBr_2\cdot 2C_3H_7Br)$.

identified[41] as $[\phi_3PR^+][\phi_3PMX_3^-]$ and $[\phi_3PR^+]_2[MX_4]^{2-}$. The metal–halogen frequencies of these complexes are virtually identical with those of the compounds $[Et_4N^+][\phi_3PMX_3^-]$ and $[Et_4N^+]_2[MX_4^{2-}]$ discussed above. Moreover the spectra of the zinc complexes indicate that they also have similar structures. Similarly, pyridine complexes may be prepared and these too may be formulated as compounds $[PyR^+]$-$[PyMX_3^-]$ on the basis of their metal–halogen frequencies[12] (Fig. 3).

Platinum and palladium complexes

Studies of square planar complexes are numerous and recent examples include the identification of the structures of cyanopyridine complexes with platinum and palladium chlorides[42] and a study of the interconversion of *cis* and *trans* diammine palladium chloride.[43]

CONCLUSION

Far-infrared spectroscopy is a rapidly expanding technique which is even now providing results of use to the inorganic and analytical chemist. It is to be expected that the future will see the continuation of the exponential growth of data presented in the literature.

Acknowledgements—The author would like to thank Professor D. W. A. Sharp for helpful discussion of much of the information presented here and Mr. K. P. Forrest for assistance with several of the spectra.

Zusammenfassung—Es gibt zahlreiche Untersuchungen über die Metall-Halogen-Schwingungsfrequenzen von Komplexen; offenbar sind solche Frequenzen oft charakteristisch für Struktur und Stöchiometrie. Obwohl allgemein anwendbar, ist die Methode von besonderem Wert, wenn weder Ultraviolettsprekten noch magnetische Momente helfen. Es wird eine Übersicht über die laufende Literatur gegeben, um die Charakterisierung unbekannter Stoffe zu erleichtern, die sich von Halogeniden zweiwertiger Metalle ableiten.

Résumé—Les études des fréquences de vibration métal-halogène de complexes sont nombreuses et il est apparent que de telles fréquences sont souvent caractéristiques de la structure et de la stoechiométrie. La méthode, quoique généralement applicable, présente le plus vif intérêt lorsque ni les spectres ultra-violets ni les moments magnétiques ne peuvent être utilisés. On passe en revue la littérature actuelle avec l'intention de faciliter la caractérisation de substances inconnues dérivés d'halogénures de métaux divalents.

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VOLUMETRIC DETERMINATION OF THE U/O RATIO IN URANIUM OXIDES

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Summary—A method is given for determining the general formula UO_{2+x} of sintered uranium dioxide pellets and uranium dioxide powders. Uranium(VI) is reduced by titration with iron(II) ammonium sulphate, after which the total amount of uranium is oxidized by titration with potassium dichromate. The end-points of both titrations are detected electrometrically. Determination of x in the range 0·0001–1·00 is possible.

IT IS important to know how the composition of nuclear fuel uranium dioxide pellets differs from the formula UO_2. Since the deviation from stoichiometry is caused by a small amount of uranium(VI), expressed by the formula UO_{2+x}, a method is needed for determining uranium(VI) in the presence of a relatively large amount of uranium(IV). As the value of x is usually small, a sensitive method should be used.

One of the most commonly used volumetric methods for the determination of uranium(VI) is the titration with titanium(III), *e.g.*, the method reported by Simmler,[1] who dissolved the oxide in phosphoric acid.

Several authors[2–4] have used coulometric methods, whereas Kubota[5] described a polarographic method for determining the stoichiometry of uranium oxide.

Spectrophotometric and gravimetric methods are also known for the determination of micro amounts of uranium(VI), but these procedures are difficult to apply to sintered uranium dioxide pellets. Gopala Rao and Seetarama Raju Sagi[6] have reported a procedure in which uranium(VI) can be determined by reduction with iron(II) ammonium sulphate in a solution of concentrated phosphoric acid. Furthermore, Gopala Rao *et al.*[7] showed that uranium(IV) can be oxidized to uranium(VI) with potassium dichromate in a phosphoric acid medium.

Because of the simplicity of this method, we adapted it to the determination of the U/O ratio in sintered uranium dioxide pellets. The pellets are sintered cylinders with a height and diameter of about 10 mm and a weight of about 10 g. This method is also applicable to the analysis of uranium dioxide powders. The method has the advantage over all others that only simple apparatus is required and that no special reagents are needed.

EXPERIMENTAL

Apparatus

Titration vessel with ground-glass head, Fig. 1.
Two platinum electrodes.
Heating-mantle, Isomantle, type PMQ 100.
Mechanical stirrer, driven by an a.c. motor.

Millivoltmeter, Philips' GM 6020 or PM 2440.
Platinum-wire basket.
Micro-burette, 1 ml, Metrohm E 374.

Reagents

Phosphoric acid. Pro analysi grade phosphoric acid.

Iron(II) ammonium sulphate solution. (*a*) 0·1*N* in 1*N* sulphuric acid, (*b*) 0·01*N* in 1*N* sulphuric acid.

Potassium dichromate. 0·1*N* in water.

Uranium(VI) solution, 1 *mg/ml.* Weigh 450 mg of *pro analysi* grade $UO_2(CH_3COO)_2{\cdot}2H_2O$, dissolve it in a few ml of water and add a few ml of concentrated sulphuric acid. Evaporate until fuming and continue heating for a further 1–2 min to remove the acetic acid. Cool, dilute with water,

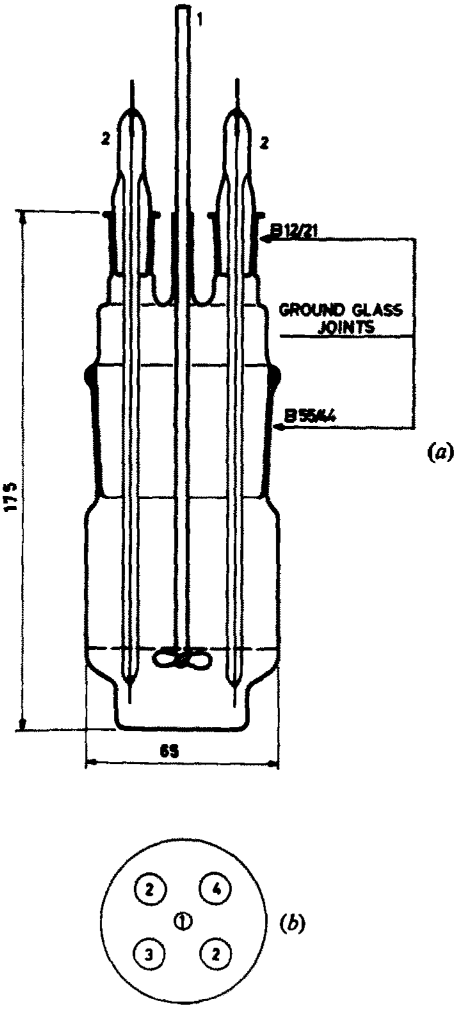


FIG. 1.—(*a*) Titration vessel with stirrer (1) and electrodes (2).
The exposed platinum parts of the electrode system are 7 mm long and 0·5-mm dia., giving a current density of 10^{-7} or 10^{-8} A/cm^2 (R = 2000 or 20,000 MΩ respectively).
(*b*) Top view of the glass head with entries for stirrer (1), electrode (2), nitrogen-inlet tube or thermometer and burette (3, 4).

transfer to a 250-ml volumetric flask, make up to the mark and mix. The solution can be standardized by a gravimetric method using 8-hydroxyquinoline or, after reduction with metallic cadmium, by titration with cerium(IV) sulphate.

Procedure

Introduce the platinum basket with the uranium dioxide pellet into the titration vessel and add 35 ml of concentrated phosphoric acid. Insert the glass head into the vessel, place the stirrer in the solution and remove the air from the solution by passing nitrogen or any other inert gas through it. Place the vessel in an electric heating-mantle and heat to 190°, while stirring, over a period of 30 min. Cool to room temperature. Take the basket with the rest of the pellet out of the solution, and remove the thermometer. Place the electrodes in the solution and take care that the stirrer is rotating just below the surface of the solution, to avoid the formation of bubbles in the viscous solution (Fig. 1*a*).

Connect the electrodes to the millivoltmeter, a 22½-V battery and two 1000-MΩ resistors (Fig. 2). If 0·01*N* iron(II) ammonium sulphate solution is used for the titration, two 10000-MΩ resistors should be used. The electrodes should have the same polarity in the circuit in successive titrations. Raise the nitrogen-entry tube, to stop the gas from bubbling through the solution, during the titration. Put the tip of the burette into the solution and stir vigorously. Titrate with 0·1*N* iron(II) ammonium sulphate solution, adding increments of 5–10 μl, and wait for about 30 sec after each addition until the potential indicated is constant. Read the millivoltmeter and plot the potentials against the added amounts of titration solution. Calculate the end-point of the titration by extrapolation (Fig. 3).

Replace the burette containing iron(II) ammonium sulphate by a burette containing 0·1*N* potassium dichromate and titrate the total amount of uranium, making a correction for the excess of iron(II) ammonium sulphate.

For the analysis of powders put a weighed amount of the sample into the titration vessel, add 35 ml of phosphoric acid and continue as above. Generally, powdered samples will be completely dissolved within the period of 30 min. The titration with potassium dichromate may be omitted, as x can be calculated from the weight of the sample and its content of uranium(VI).

Calculation

The weight of UO_{2+x} dissolved is given by the equation

$$g = 0{\cdot}135a_2 + 0{\cdot}008a_1$$

and the value of x by the equation

$$x = a_1/a_2$$

where g is the weight of the sample in grams, a_1 is the number of mequiv of iron(II) ammonium sulphate used in the first titration, and a_2 is the number of mequiv of potassium dichromate used in the second titration. If a weighed powdered sample is dissolved and titrated with iron(II) ammonium sulphate only, x is given by

$$x = \frac{0{\cdot}270a_1}{2g - 0{\cdot}016a_1}.$$

These calculations are based on the atomic weight of natural uranium.

Blanks and interferences

When *pro analysi* grade phosphoric acid was taken through the procedure, the blanks were found to be less than 10 μl of 0·01*N* iron(II) ammonium sulphate.

Iron(II), and other components that change the oxidation states of uranium when the oxide is dissolved, must be absent. Specifications for reactor-grade uranium dioxide usually set the limit for the presence of other elements so low that there is no significant influence on the amounts of titrants used.

DISCUSSION AND RESULTS

Uranium(VI) can be reduced to uranium(IV) in a concentrated phosphoric acid medium by titration with a solution of iron(II) ammonium sulphate, and the end-point can be detected potentiometrically with a millivoltmeter and a saturated calomel electrode–platinum electrode system. However, a much better end-point was obtained when two platinum electrodes and a constant current of about 10^{-8} A were used.

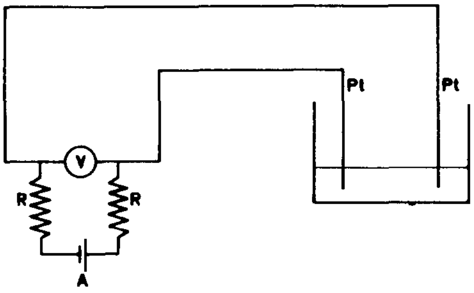
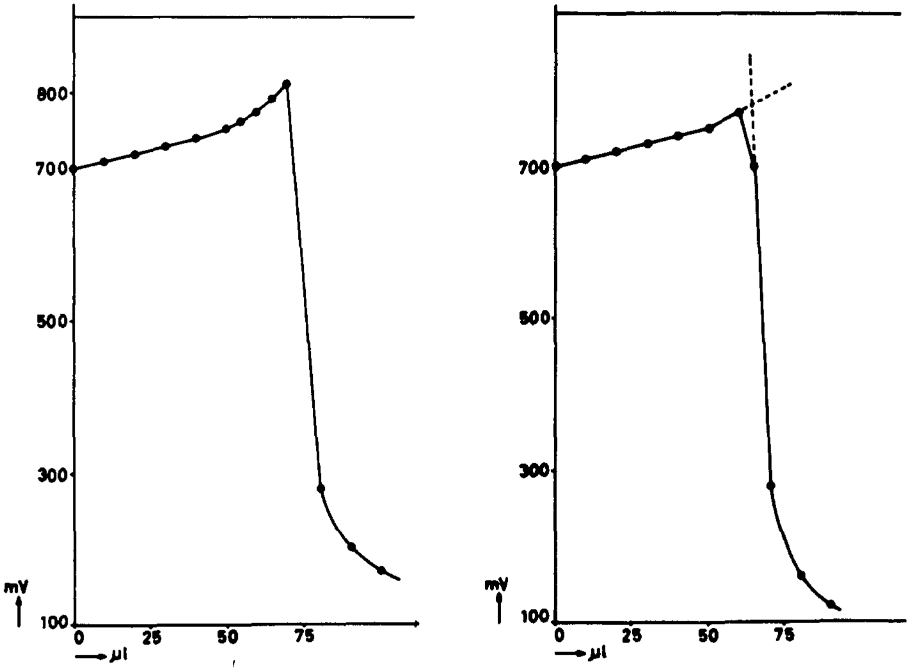


Fig. 2.—Circuit diagram for measuring the potential of the solution.
Pt—platinum electrodes; *A*—22½-V battery; *R*—1000 or 10,000 MΩ resistor;
V—Philips' GM 6020 millivoltmeter.

A good stirring system was essential because of the viscosity of the solution. It was found that a magnetic stirrer was inadequate and that a mechanical stirrer with a rotating glass rod, placed vertically in the solution, was more effective. Because spatter of the syrupy phosphoric acid on the non-immersed parts of the electrodes disturbed the measurement of the potential, the electrodes were partly sealed in glass tubes; the inner walls of these tubes must be absolutely dry (Fig. 1*a*). It was found important that the exposed electrode should have an area that would give a favourable current density (~10^{-7} A/cm^2).

To avoid the formation of bubbles in the viscous solution and on the electrodes,



(a) (b)

Fig. 3.—Titration curves: (*a*) is the ideal form, from which the end-point can be read directly; from a curve like (*b*) the end-point must be extrapolated.

the stirrer should be rotated just below the surface of the solution, and the electrodes dipped into the solution to such a depth that the exposed parts of the electrodes are about 15 mm from the stirrer. For optimum conditions it was found necessary to heat the phosphoric acid to 190 ± 5° over a period of 30 min and then to cool it, otherwise the indication of the potential during the titration was very unsatisfactory. The viscosity of the solution became too great if the temperature was raised above 190°.

During the heating of the phosphoric acid the sample to be analysed must dissolve. However, the reaction between sintered uranium dioxide and phosphoric acid was very slow and the splintered pellet would not dissolve quantitatively within the prescribed 30 min. Pulverizing the pellet in an air atmosphere was not possible because it would result in serious oxidation of the sample. The effect of grinding on the analysis was investigated as follows. A uranium dioxide pellet was pulverized in a mortar and a 515-mg sample taken to determine the value of x; x was found to be 0·0039. To see whether there was any difference between fine and coarse particles, the sample was sieved; 508 mg of fine and coarse particles were taken and x was found to be 0·0069 and 0·0010 respectively. The fine sample was ground further and the value of x increased to 0·010. We therefore tried to pulverize the pellets in an inert atmosphere in a glove box, but we found it very troublesome to obtain a powder sufficiently fine to be dissolved within the required 30 min.

TABLE I.—CHANGE IN x FROM THE SURFACE OF A PELLET TO ITS INTERIOR; IN ALMOST ALL CASES THE VALUE OF x BECAME CONSTANT AFTER 2–4 DETERMINATIONS

No	Sample dissolved, *mg*	Thickness of the layer, *mm*	x
1	548	0·13	0·0059
2	450	0·11	0·0019
3	351	0·09	0·0016
4	588	0·17	0·0013
5	120	0·04	0·0012
6	500	0·16	0·0012
7	225	0·07	0·0012
8	734	0·26	0·0012
9	350	0·14	0·0012
10	376	0·17	0·0012

To overcome these difficulties the following procedure was used. A platinum basket containing the pellet to be analysed was introduced into the phosphoric acid. During the heating period some uranium dioxide from the surface of the pellet was dissolved. The amount of uranium(VI) in the solution was determined by titration with iron(II) ammonium sulphate, after which the total amount of uranium was determined by titration with potassium dichromate. This procedure has the additional advantage that the pellet can be used a number of times to determine how the value of x varies from the outer to the inner parts of the pellet. In this way the average value of x in different layers can be determined and the thickness of the layer calculated (Table 1).

Atmospheric oxidation of the pellets can be ignored. Pellets analysed in this way until x became constant were rinsed with water and alcohol and dried in a current of air from a blower. These samples were analysed again after 24 hr and one week and no increase in the value of x was found.

Powders with various x-values were analysed. For pure U_3O_8 samples x was found to be 0·66–0·67, and in UO_3 powders x was found to have the theoretical value 1·00. The method was controlled by the addition of varying amounts of the standardized uranium(VI) solution to phosphoric acid in which pellets with a constant x-value had previously been treated. Between 0·1 and 2 ml of the uranium(VI) solution were added to phosphoric acid, treated as described, and the amount of uranium(VI) was determined. The relative error of the method varies from 1–10%, depending on the amount of uranium(VI) in the solution. Very low values of x can be determined by titration with 0·01N iron(II) ammonium sulphate. However, it is then advisable to use a current of 10^{-9} A. Values for x as low as 0·0001 were investigated; at this level, interference from impurities may become significant. In this laboratory the method has been used for several years with good results.

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Zusammenfassung—Eine Methode zur Ermittlung der allgemeinen Formel UO_{2+x} gesinterter Urandioxidtabletten und -pulver wird angegeben. Uran(VI) wird durch Titration mit Eisen(II)-ammonsulfat reduziert und anschließend das gesamte Uran durch Titration mit Kaliumdichromat oxidiert. Die Endpunkte beider Titrationen werden elektrometrisch angezeigt. Die Bestimmung von x ist möglich im Bereich 0,0001–1,00.

Résumé—On donne une méthode pour déterminer la formule générale UO_{2+x} des pastilles de bioxyde d'uranium fritté et des poudres de bioxyde d'uranium. On réduit l'uranium(VI) par titrage au sulfate de fer(II) et d'ammonium, après quoi on oxyde la totalité de l'uranium par titrage au bichromate de potassium. Les points de fin de réaction des deux titrages sont décelés électrométriquement. La détermination de x est possible dans le domaine 0,0001 à 1,00.

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STUDIES ON IMIDAZOLE DERIVATIVES AS CHELATING AGENTS—IV*

STABILITY CONSTANTS OF THE METAL CHELATES OF AZOIMIDAZOLES

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Summary—Chelating abilities of several azoimidazoles containing a hydroxy and/or a dimethylamino group, and the structures of their copper chelates, were investigated. 1-(5-Methyl-4-imidazolylazo)-2-naphthol(IAN) formed a brown-black chelate having the composition Cu(ligand)Br whereas 4-(5-methyl-4-imidazolylazo)dimethylaminobenzene (DAI) formed a reddish brown chelate Cu(ligand)$_2$Br$_2$·2H$_2$O. The contribution of the phenolic OH and the imino NH group to the binding with copper is discussed from the infrared spectra. The metal: ligand ratios of the Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) chelates were determined by the method of continuous variations and their stability constants were determined at 25° in 50% v/v dioxane–water by the Bjerrum-Calvin method. The OH-containing azoimidazoles were found to form stable chelates with log K_1K_2 values 14·9–25·4 and the stabilities approximately followed the Mellor-Maley stability sequence. The compound DAI, which has no OH group, formed weak chelates with Co(II), Ni(II) and Cu(II).

Studies have been reported on the chelating abilities of many *o*-hydroxyphenylazo compounds with such heterocycles as pyridine and thiazole, and they play a very important part in the prediction of the applicabilities of the azo compounds as analytical reagents. From the remarkable colour reactions of the azoimidazoles, which were reported in a previous paper,[1] it is expected that they may be useful analytical reagents for metal ions. In order to make comparison of the chelating abilities of the azoimidazoles with those of the existing reagents, such as 1-(2-pyridylazo)-2-naphthol(PAN) and related compounds, and to estimate their analytical applicabilities, the stability constants of several metal chelates of the azoimidazoles were determined by the potentiometric method, and the contribution of the phenolic OH and the imino NH group to binding with copper was deduced from the infrared spectra.

The present paper deals with the discussion of the structures and the stability constants of the metal chelates.

EXPERIMENTAL

Reagents

Azoimidazoles. The following four azoimidazoles[1] were used: 1-(5-methyl-4-imidazolylazo)-2-naphthol (IAN); 2-(5-methyl-4-imidazolylazo)-4-methoxyphenol (IAM); 2-(5-methyl-4-imidazolylazo)-4-dimethylaminophenol (DIP); 4-(5-methyl-4-imidazolylazo)dimethylaminobenzene (DAI).

Standard metal solutions, 0·01*M*. Prepared by dissolving cobalt nitrate, nickel sulphate, copper

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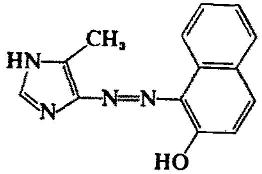
nitrate, zinc nitrate, cadmium nitrate, manganese acetate and lead acetate in water, and standardized by titration with EDTA, itself standardized with zinc (99·99% pure).

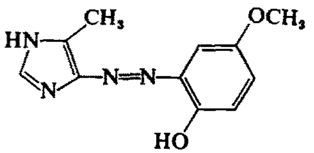
Carbonate-free 0·1M *potassium hydroxide.* Prepared by the method of Armstrong[3] and standardized against potassium hydrogen phthalate.

Nitric acid 0·1M. Standardized against 0·1M potassium hydroxide.

All the reagents used were of reagent grade. Deionised water was used throughout.



IAN



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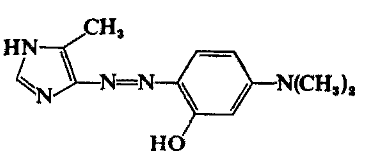
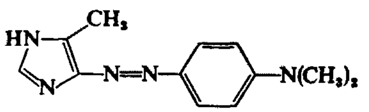


DIP



DAI

Apparatus

Spectrophotometer. Hitachi Model EPS-2U recording spectrophotometer.

pH Meter. Radiometer Titrator TTT1 and Titrigraph equipped with a Radiometer G202B glass electrode and a K401 saturated calomel electrode.

Isolation of the copper chelates

Cu(II)–IAN. Copper(II) nitrate trihydrate (70 mg) in 10 ml of aqueous ethanol was added to a solution of IAN (75 mg) in 10 ml of ethanol, and a 10% aqueous solution of potassium bromide was added dropwise to the mixture until the precipitation of the chelate was complete. The precipitate was filtered off, washed with aqueous ethanol and dried at 100° over phosphorus pentoxide to yield brown-black crystals, m.p. 285° (decomp.). (Found: C, 42·9%; H, 3·0%; N, 14·3%; O, 4·2%: $C_{14}H_{11}N_4OBrCu$ requires: C, 42·60%; H, 2·81%; N, 14·20%; O, 4·05%.)

Cu(II)–DAI. This was obtained similarly from DAI (60 mg) and copper(II) nitrate trihydrate (30 mg) and recrystallized from methanol–ethanol to yield reddish brown crystals, m.p. 182–183° (decomp.). (Found: C, 40·5%; H, 5·0%; N, 19·3%: $C_{24}H_{30}N_{10}Br_2Cu{\cdot}2H_2O$ requires: C, 40·15%; H, 4·77%; N, 19·52%.)

Titration procedure

The pH titration procedure was essentially the same as that reported previously.[2] The azoimidazole (10–20 mg), accurately weighed, was dissolved in 5 ml of purified dioxane, to which 1 or 2 ml of 0·1*M* nitric acid, 1 ml of 1*M* potassium nitrate solution and 1 ml of 0·01*M* metal ion solution were added, and the total volume was adjusted to 10 ml by adding water. The mixture was titrated with 0·1*M* potassium hydroxide at 25° under a nitrogen atmosphere, and the pH values were measured. The composition of the solvent was kept constant by adding equal volumes of 0·1*M* potassium hydroxide and dioxane at the same time through a twin burette.

Calibration of the pH meter and determination of the apparent ion-product of water in 50% v/v dioxane–water

The calibration was made according to Van Uitert and Haas.[4] The difference, *C*, between the calculated $-\log[H^+]$ and the pH meter reading pH_m, when 0·1*M* potassium nitrate in 50% v/v dioxane–water was titrated with 0·1*M* nitric acid under the conditions described above was found to be −0·12; $C = -\log[H^+] - pH_m$ where $[H^+]$ is the calculated stoichiometric concentration of hydrogen ions.

The apparent ion-product of water, K_w', was obtained by titrating 0·1*M* potassium nitrate in 50% v/v dioxane–water with 0·1*M* potassium hydroxide under the same conditions, and the value of pK_w' was calculated to be 15·40 according to the equation

$$pK_w' = -\log[H^+] - \log[OH^-]$$

where $[OH^-]$ is the calculated stoichiometric concentration of hydroxyl ions.

RESULTS AND DISCUSSION

Metal:ligand ratios

Since the OH-containing azo compounds IAN, IAM and DIP are considered to react with metal ions in a similar fashion while DAI reacts differently, IAN and DAI were chosen as typical compounds, and as a basis for the calculation of the stability constants. The metal:ligand ratios of their chelates were determined by the method of continuous variations at the wavelengths of maximum absorption. The results are summarized in Table I.

TABLE I.—METAL:LIGAND RATIOS DETERMINED BY THE METHOD OF CONTINUOUS VARIATIONS IN 50% V/V ETHANOL–WATER

Ligand	Metal ion	pH	λ, mμ	Metal:ligand
IAN	Co(II)	5·8	550	1:2
	Ni(II)	5·8	518	1:2
	Cu(II)	6·0	532	1:1
	Cu(II)	8·1	532	1:1
	Zn(II)	8·1	512	1:2
	Cd(II)	9·3	510	1:2
DAI	Co(II)	6·8	530	1:3
	Ni(II)	6·5	530	1:3
	Cu(II)	6·0	550	1:2

The absorption spectra of IAN at pH values above 4·5 in the presence of one of the metal ions such as Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) showed strong absorptions in the region 510–560 mμ as a result of complex formation. These absorptions disappeared at lower pH values (below 2·5). The molar absorptivities of the copper and cadmium chelates were $2{\cdot}0 \times 10^4$ and $3{\cdot}8 \times 10^4$, respectively. The spectra of DAI in the presence of metal ions were essentially the same as the spectrum of DAI alone except that the absorptions in the region 500–550 mμ increased owing to complexation.

The compound IAN was found to form 1:2 chelates with Co(II), Ni(II), Zn(II) and Cd(II) and a 1:1 chelate with Cu(II). The ratios for the cobalt, nickel and copper chelates are in agreement with the values reported for PAN[5] and 4-(2-pyridylazo)-resorcinol (PAR),[6] but the ratios for the zinc and cadmium chelates are different from those reported for PAR by Iwamoto.[6] On the basis of the spectra, Wada and Nakagawa[7] reported the formation of 1:2 copper chelates of PAN and PAR at a pH above 10. The compound IAN might be expected to form a 1:2 chelate with Cu(II), but the present investigations at pH 6·0 and 8·1 indicated the formation of the 1:1 chelate.

Structures of the copper chelates

Inasmuch as the OH and NH groups of the *o*-imidazolylazophenols are supposed to have the ability to combine with metals, it is necessary to clarify which of the two groups contributes to the binding with metals under the experimental conditions used.

The compounds IAN and DAI form copper chelates of the compositions Cu(ligand)Br and Cu(ligand)$_2$Br$_2$·2H$_2$O, respectively. The presence of bromide ions in the chelates indicates that in the Cu(II)–IAN chelate only one of the two groups (NH and OH) is involved in the binding with the copper atom, whereas the binding in the Cu(II)—DAI chelate apparently does not involve the NH group. The infrared spectrum of the Cu(II)–IAN chelate, shown in Fig. 1, exhibits a band at 3190 cm^{-1} which may be attributed either to the N–H of the imidazole ring or to the O—H of the phenolic moiety, and the broad absorptions of the ligand in the region 2500–3000 cm^{-1} are not observed. Deuteration of the chelate gives a band near 2380 cm^{-1}, and causes a frequency shift in the region 1400–1450 cm^{-1} where the stretching frequencies of the imidazole ring are to be found.[8] That the deuteration affects the ring stretching frequencies may be indicative of the formation of the N—D bond and consequently the presence of the NH group. The view is also supported by the pK_a values of the OH and NH groups of IAN and DAI[8] and the binding site found in the Cu(II)–DAI chelate. Binding through the OH group may also be presumed to take place on complex formation with the other transition metals. Concerning the co-ordination of the azo group of PAR, Geary *et al.*,[9] by comparing the colour reactions of PAR and some structurally related compounds concluded that the nitrogen atom farthest from the pyridine ring made the greater contribution. In the previous paper,[10] the greater reactivities of the Schiff bases (a) with metals as compared with the Schiff bases (b) were attributed to the ability of the a-type Schiff bases to form a five-membered chelate ring (Fig. 2).

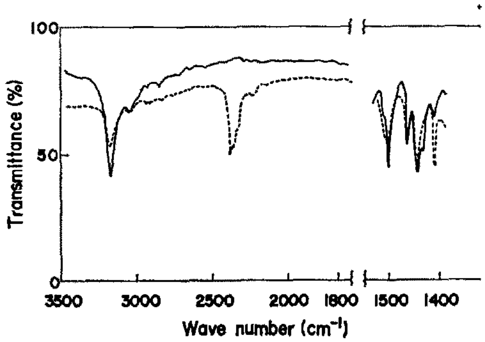
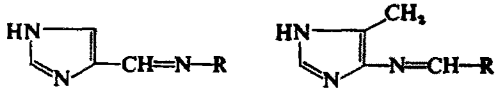


FIG. 1.—Infrared spectra of the Cu(II)–IAN chelate and its deuteration product (HCB mull).
——— Non-deuterated.
- - - - Deuterated.
The chelate could not be deuterated completely owing to insufficient solubility in dioxane–deuterium oxide.



(a) (b)

FIG. 2.—Structures of the Schiff bases.

Because IAN and DAI seem to be structurally comparable with PAR and the Schiff bases, the considerations above are probably applicable to the present cases, and the complexing groups may be considered to be the pyridine-like nitrogen, the azo nitrogen farthest from the imidazole nucleus, and the OH group. Although the charge of the Cu(II) ion is not neutralized completely, the Cu(II)–IAN chelate is soluble in chloroform and isoamyl alcohol and almost insoluble in water, whereas the Cu(II)–DAI chelate is soluble both in chloroform and water.

Stability constants

The chelating abilities of the azoimidazoles were investigated according to the Bjerrum-Calvin method.[11–13] As they are considered to be dibasic acids in the pH ranges used for the calculations of the constants (Table II), the concentration of free ligand, [L], and the average number of ligand molecules bound to a metal atom, $\bar{n}$, were calculated by means of the following equations[13,14]

TABLE II.—pH RANGES FOR THE CALCULATIONS OF THE STABILITY CONSTANTS

Metal ion	Ligand			
	IAN	IAM	DIP	DAI
Co(II)	2·6–4·0	2·7–3·6	2·7–4·1	2·5–4·9
Ni(II)	2·3–3·8	2·4–3·6	2·4–4·1	2·4–5·7
Cu(II)	2·1–3·7	2·1–3·4	2·2–4·0	2·2–3·8
Zn(II)	2·6–4·5	3·1–6·7	3·0–5·1	
Cd(II)	2·8–5·7	2·6–7·2	2·6–4·9	

$$[\mathrm{L}] = \frac{[\mathrm{L_0}] + [\mathrm{HNO_3}] - [\mathrm{KOH}] - [\mathrm{H^+}] + [\mathrm{OH^-}]}{\dfrac{[\mathrm{H^+}]}{k_2} + \dfrac{2[\mathrm{H^+}]^2}{k_2 \cdot k_1}} \cdot$$

$$\bar{n} = \frac{[\mathrm{L_0}] - [\mathrm{L}]\left\{1 + \dfrac{[\mathrm{H^+}]}{k_2} + \dfrac{[\mathrm{H^+}]^2}{k_2 \cdot k_1}\right\}}{[\mathrm{M_0}]}$$

where $[\mathrm{L_0}]$ and $[\mathrm{M_0}]$ are the total concentrations of ligand and metal, respectively, and k_1 and k_2 are the acid dissociation constants of the ligand.[3]

On the basis of the structures of the copper chelates described above, the binding with metals through the OH group of IAN, IAM and DIP was taken into account and the contribution of the NH group to the binding was neglected.

The stability constants were calculated from 15–50 sets of $\bar{n}$ and −log [L] (pL) by using the method of least squares.[15] When the chelates had a metal : ligand ratio of 1:3, the results were calculated from half $\bar{n}$ values with or without refining by the method of successive approximations.[15,16] Owing to the low solubilities of the chelates, precipitation occurred during every titration, so that complete formation curves could not be obtained. In some cases there were abnormal decreases in the $\bar{n}$ values beginning at a point near pH 4 and the values then increased again gradually. For these reasons, some stability constants were obtained only from limited pH ranges and are of less validity. All the calculations were made with the use of the KDC-II

(Hitachi HITAC 5020) digital computer of the Kyoto University Computation Centre. The titration data for the copper chelates of IAN, IAM and DIP suggest a metal : ligand ratio of 1 : 2 that does not agree with the result of continuous variations, and the treatment of the data by the method of least-squares gave the log β_2 values, which are shown in parenthesis for comparison. This discrepancy may arise from the possible dissociation of the NH group of the imidazole nucleus, facilitated by the presence of Cu(II) ions. However, Geary *et al.*[17] also reported the log K_1 and log K_2 values for the Cu(II)–PAR chelate, for which the metal : ligand ratio was determined to be 1 : 1 by the method of continuous variations.[6] The stability constants are summarized in Table III.

TABLE III.—STABILITY CONSTANTS OF THE METAL CHELATES OF THE AZOIMIDAZOLES IN 50% V/V DIOXANE–WATER AT 25 ± 0·1°C (0·1M KNO$_3$)

Ligand*		Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
IAN	log K_1	13·0	12·9	14·1	11·6	10·4
	log K_2		11·8	(10·9)†	9·7	8·0
	log β_2		24·7	(25·0)†	21·3	18·4
IAM	log K_1	11·2	11·8	13·3	10·0	8·4
	log K_2	10·2	9·9	(11·3)†	6·9	6·5
	log β_2	21·4	21·7	(24·6)†	16·9	14·9
DIP	log K_1	12·8	13·9	14·5	11·7	12·3
	log K_2	11·5	11·5	(11·5)†	9·6	9·3
	log β_2	24·3	25·4	(26·0)†	21·3	21·6
DAI	log K_1	4·2	5·0‡	5·0		
	log K_2	4·3	4·7‡	6·4		
	log K_3	4·2	4·4‡	—		
	log β	12·7	14·1	11·4		

* The pK_a values in 50% v/v dioxane–water at 25 ± 0·1° are:[3]
IAN: pK_{a1} = 3·8; pK_{a2} = 11·6
IAM: pK_{a1} = 3·9; pK_{a2} = 11·0
DIP: pK_{a1} = 4·9; pK_{a2} = 11·8
DAI: pK_{a1} = 1·3; pK_{a2} = 5·1.

† Shown for comparison because the results of continuous variations indicate the formation of 1 : 1 chelates.

‡ Obtained from the formation curve by the relationship $\log K_n = \mathrm{pL}\bar{n}$ where $\bar{n} = n - \frac{1}{2}$.

It is apparent from the table that the *o*-hydroxyphenylazo derivatives IAN, IAM and DIP form very stable chelates. Their Ni(II), Cu(II) and Zn(II) chelates are slightly less stable than the corresponding chelates of PAN[18,19] but much more stable than those of the related *o*-thiazolylazophenols.[20] Their stabilities are comparable with those of the chelates of 4-(2-thiazolylazo)resorcinol.[21] Of the four ligands, DIP forms the most stable chelates with all the metals studied. The stabilities fall in the order DIP > IAN > IAM > DAI, and this may be explained in terms of the pK_a values of the complexing groups of the ligands. The log K_1 values of the chelates of IAN, IAM and DIP approximately follow the Mellor–Maley stability sequence.

On the other hand, the compound DAI, which has no OH group, forms weak chelates with Co(II), Ni(II) and Cu(II) (log β = 11–14). The log K_1 values are comparable with those reported for 2-(*p*-dimethylaminophenylazo)pyridine[22] which has a structure closely resembling that of DAI. When the stabilities of these chelates are compared with those of the IAN, IAM or DIP chelates, the strong effect of the OH group on the chelate stability is readily perceived.

Generally the log K_1 values are greater than the log K_2 values except that the log K_1/K_2 values of the Cu(II)–DAI and Co(II)–DAI chelates are −1·4 and −0·1, respectively, and formation of 1:1 chelates is therefore preferred to that of 1:2 chelates. As the *o*-imidazolylazophenols are considered to be terdentate ligands, the preferred formation of 1:1 chelates may be due to the steric requirements around the central metal atom.

It is expected from the stability constants that IAN, IAM and DIP would be good metallochromic indicators in chelatometric titrations with ethylenediaminetetraacetic acid (EDTA) as titrant, because, so far as their 1:1 chelates are concerned, they are sufficiently stable but not as stable as those of EDTA. Although the standard deviations of the log β_2 values for some chelates (0·5–1) are somewhat larger than usual, the constants may be of value in estimating their analytical applicabilities.

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Zusammenfassung—Die Fähigkeit einiger Azoimidazole mit einer Hydroxy- und bzw. oder einer Dimethylaminogruppe zur Chelatbildung sowie die Struktur ihrer Kupferchelate wurden untersucht. 1-(5-Methyl-4-imidazolylazo)-2-naphthol (IAN) bildete ein braunschwarzes Chelat der Zusammensetzung Cu(Ligand)Br, 4-(5-Methyl-4-imidazolylazo)dimethylaminobenzol (DAI) hingegen ein rötlichbraunes Chelat Cu(Ligand)$_2$Br$_2$·2H$_2$O. An Hand der Infrarotspektren wird die Beteiligung der phenolischen OH- und der Imino-NH-Gruppe an der Bindung mit dem Kupfer diskutiert. Die Metall:Ligand-Verhältnisse der Chelate von Co(II), Ni(II), Cu(II), Zn(II) und Cd(II) wurden mit der Methode der kontinuierlichen Variationen ermittelt, die Stabilitätskonstanten bei 25° in 50% (Volumen) Dioxan-Wasser nach der Methode von Bjerrum und Calvin. Die OH enthaltenden Azoimidazole bilden stabile Chelate mit log K_1K_2 von 14,9 bis 25,4, die Stabilitäten folgen ungefähr der Sequenz von Mellor und Maley. DAI, das keine OH-Gruppe besitzt, bildet schwache Chelate mit Co(II), Ni(II) und Cu(II).

Résumé—On a étudié les aptitudes chélatantes de plusieurs azoimidazoles contenant un groupe hydroxy et/ou un groupe diméthylamino, et les structures de leurs chélates avec le cuivre. Le 1-(5-méthyl 4-imidazolylazo)2-naphtol (IAN) forme un chélate brun-noir ayant une composition Cu(ligand)Br tandis que le 4-(5-méthyl 4-imidazolylazo)diméthylaminobenzène (DAI) forme un chélate brun rougeâtre Cu(ligand)$_2$Br$_2$, 2H$_2$O. A partir des spectres infra-rouges, on discute de la contribution du OH phénolique et du groupe NH imino à la liaison avec le cuivre. On a déterminé les rapports métal:ligand des chélates de Co(II), Ni(II), Cu(II), Zn(II) et Cd(II) par la méthode des variations continues et leurs constantes de stabilité ont été déterminées à 25° en dioxane-eau 50% v/v par la méthode de Bjerrum-Calvin. On a trouvé que les azoimidazoles possédant OH forment des chélates stables avec des valeurs de log K_1K_2 de 14,9–25,4 et les stabilités suivent approximativement la séquence de stabilité de Mellor-Maley. Le composé DAI, qui ne possède pas de groupe OH, forme des chélates faibles avec Co(II), Ni(II) et Cu(II).

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GRAVIMETRIC DETERMINATION OF CAESIUM AND POTASSIUM WITH SODIUM TRIPHENYLCYANOBORATE (CAESIGNOST)

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Summary—Caesium can be determined gravimetrically with sodium triphenylcyanoborate (Caesignost) as precipitant. The precipitation was checked by addition of ^{137}Cs tracer and gamma-spectrometry. The following parameters were studied: temperature, digestion time, influence of potassium on the precipitation of caesium, and separation of caesium from bulk quantities of potassium.

SODIUM triphenylcyanoborate is prepared[1] by heating sodium-tetraphenylborate with sodium cyanide. The reactions of sodium triphenylcyanoborate (Caesignost) were studied by Havir[2] with special emphasis on electrometric methods. He succeeded in determining caesium qualitatively and quantitatively in small amounts. Under his experimental conditions potassium did not precipitate at all. The present investigation was undertaken to check the usefulness of Caesignost as a precipitant for caesium and potassium individually and for caesium in the presence of large quantities of potassium. It was also intended to test its applicability to radiochemical separation. Radioactive tracer technique was used to develop the procedure. The procedure of Havir served as a starting point, but larger samples were used.

EXPERIMENTAL

Reagents

Solutions of caesium and potassium were prepared from CsCl, $CsNO_3$, KCl and KNO_3. The concentration of caesium was determined gravimetrically by precipitation as $CsBi_2I_9$ and of potassium by precipitation as potassium tetraphenylborate.

Caesignost—sodium triphenylcyanoborate (Heyl & Co., Berlin)—was prepared as a 7% aqueous solution. If a turbidity appears, clarification by addition of 1 g of alkali-free aluminium hydroxide is recommended. If, during the clarification, the first portions passing through the filter-paper (Schleicher & Schuell SS 595) are still turbid, the solution must be refiltered several times.

Blanks were run from time to time. All the reagents used were analytical grade.

Radioisotope

^{137}Cs, $t_{1/2} = 30y$, measured *via* 2·6-min ^{137}Ba by gamma-counting at 662 keV with a 4 × 4 in. NaI(Tl) crystal and a 256-channel analyser.

Procedure for caesium

A preliminary study was undertaken to determine the appropriate concentration of Caesignost and acidity of the solution which would result in quantitative separation of a precipitate with desirable physical characteristics. The same procedure was used in all the comparison tests. The conversion factor is 0·331.

Different amounts of caesium (20–50 mg) were precipitated with Caesignost at room temperature. The pH of the solution was adjusted to 3, the experimentally found optimum, with hydrochloric or nitric acid. A stoichiometric excess of 7% Caesignost solution was added, with stirring. A white precipitate was formed and allowed to stand overnight. After collection on a porosity 4 sintered glass filter, the precipitate was washed twice with 1% Caesignost solution and twice with 2 ml of cold water. It was dried for 1 hr at 105°, cooled and weighed. The precipitate is most soluble in acetone. The results were evaluated statistically and given in Tables 1 and 2. The results indicate little or no difference in the precipitation in chloride and nitrate media. As shown in Tables I and II satisfactory results can be obtained with 20–50 mg of caesium, though the relative error is large. Larger amounts up to 400 mg were also determined, with similar results. A difference in the precipitation yield due to variations in room temperature was observed. Therefore the next objective of investigation was to find the optimal temperature range for the precipitation.

TABLE I.—DETERMINATION OF CAESIUM IN CHLORIDE MEDIUM

Cs added, *mg*	Cs found,* *mg*	Standard deviation, *mg*	Coefficient of variation, %
20·0	19·72	1·41	7·1
30·0	29·70	1·71	5·6
40·0	39·80	1·95	5·0
50·0	49·60	1·99	4·0

* Mean value of 10 results.

TABLE II.—DETERMINATION OF CAESIUM IN NITRATE MEDIUM

Cs added, *mg*	Cs found,* *mg*	Standard deviation *mg*	Coefficient of variation, %
20·0	19·60	1·40	7·1
30·0	29·90	1·73	5·8
40·0	39·75	1·98	5·0
50·0	49·80	2·24	4·5

* Mean value of 10 results.

TABLE III.—PRECIPITATION OF CAESIUM AT DIFFERENT TEMPERATURES

Temperature, °*C*	Cs taken, *mg*	Cs found,* *mg*	Standard deviation *mg*
15–25	20·0	19·72	±1·40
30	20·0	16·40	±3·41

* Mean value of 20 results

The standard deviation of the results obtained at 30° was very large. It is therefore suggested that the precipitation should be made at room temperatures not exceeding 25°.

Caesium was then precipitated at room temperature but the time of digestion was limited to 30 min. The results are given in Table IV, and are much improved.

TABLE IV.—PRECIPITATION OF CAESIUM AFTER 30-MIN DIGESTION

Cs added, *mg*	Cs found, *mg*	Standard deviation, *mg*
20·0	19·90	±0·19
50·0	49·80	±0·22

Procedure for potassium

Since Havir[2] got no precipitate with limited quantities of potassium, his experiments were repeated and extended by precipitating 10–50 mg and 50–1000 mg of potassium under the same conditions as for caesium. In both cases precitation remained incomplete. The results are given in Table V.

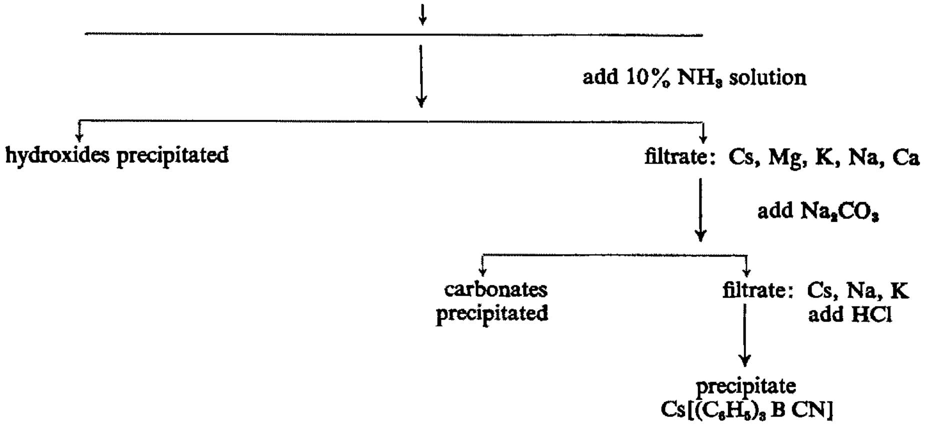
TABLE V.—DETERMINATION OF POTASSIUM

Time of digestion, *hr*	K added, *mg*	K found, *mg*
12	50·0	15·7
	400	136·0
	1000	298·0
0·5	50·0	nil
	400	nil
	1000	nil

Procedure for caesium in the presence of potassium

To determine the behaviour of caesium in solution in the presence of various amounts of different salts of potassium, a synthetic model with rough resemblance to vegetation or biological material was prepared and used throughout the experiment. The composition of the synthetic model was NH_3 = 10 mg; Ca^{2+} = 140 mg; Cl^- = 330 mg; K^+ = 200 mg; Fe^{3+} = 7 mg; SO_4^{2-} = 20 mg; Na^+ = 130 mg; Mg^{2+} = 10 mg; PO_4^{3-} = 60 mg; in 100 ml of demineralized water. Each sample had 20 mg of caesium added and was spiked with 2×10^3 pCi of ^{137}Cs. The separation was carried out according to the scheme:

100 ml of model solution + 20 mg of Cs-carrier + 2000 pCi of ^{137}Cs + KCl



From the γ-ray spectrum and weight of the precipitate no contamination with potassium was evident. The final precipitate was dissolved in acetone and the caesium was reprecipitated. The results are presented in Table VI.

TABLE VI.—PRECIPITATION OF CAESIUM IN THE PRESENCE OF LARGE QUANTITIES OF POTASSIUM

KCl added, *g*	Yield, %		Potassium co-precipitated, %
	Gamma-spectrometry	Gravimetric	
0	98·8	98·3	—
5	59·6	59·4	—
10	59·4	59·4	—

The necessary conditions were obtained by shortening the maximum time of digestion to 30 min, thus avoiding co-precipitation of potassium. It seems that further addition of potassium has no influence on the precipitation.

DISCUSSION

Caesignost undergoes a decomposition which has not yet been explained. In a period varying from a few hours to several weeks the solution may become turbid, progressively developing a strong phenolic odor.

It also appears that the presence of the decomposition products may speed further deterioration. As mentioned before, the first portions of filtered reagent are usually turbid and must be refiltered several times. By analogy with sodium tetraphenylborate[4] the filtrate was clarified by addition of a trace of a caesium salt. The precipitate serves as a carrier for the very fine particles causing the turbidity, and in the process the filtrate is saturated with caesium triphenylcyanoborate. A pH higher than 7 should be avoided. The alumina treatment yields a solution of pH 4–5. The precipitation of caesium is complete under the chosen conditions. The gravimetric technique was used because of its simplicity and convenience. The coarseness of the precipitate was found to depend on the pH of the solution. The precipitation of potassium does not occur immediately, even on stirring, as it does in the case of caesium, but starts after 1 hr, which is an advantage when separating caesium in the same solution. The white precipitate of potassium triphenylcyanoborate is not as coarse as that of caesium triphenylcyanoborate.

The precipitation of caesium in the presence of small amounts of potassium up to 200 mg is not impeded if the time of digestion is limited to 30 min. Larger quantities of potassium (up to 5·0 g) do not co-precipitate, but interfere with quantitative precipitation of caesium. Addition of ammonia does not interfere with the precipitation of caesium.

Sodium triphenylcyanoborate can be recommended as a precipitant for caesium in radiochemical analysis, especially for the separation of ^{137}Cs in fall-out[5] in the presence of negligible amounts of potassium, and in samples of vegetation and sea-water[3] where the ratio K:Cs-carrier may exceed 200.

Zusammenfassung—Caesium kann gravimetrisch mit Natriumtriphenylcyanoborat (Caesignost) als Fällungsmittel bestimmt werden. Die Fällung wurde durch Zusatz von ^{137}Cs als Tracer und Gamma-Spektrometrie geprüft. Folgende Parameter wurden untersucht: Temperatur, Absitzzeit, Einfluß von Kalium auf die Caesiumfällung und Abtrennung von Caesium von großen Kaliumüberschüssen.

Résumé—On peut doser le caesium gravimétriquement en utilisant le triphénylcyanoborate de sodium (Caesignost) comme agent de précipitation. On a contrôlé la précipitation par addition de traceur ^{137}Cs et par spectrométrie gamma. On a étudié les paramètres suivants: température, temps de digestion, influence du potassium sur la précipitation du caesium, et séparation du caesium de quantités considérables de potassium.

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THE SYSTEM ALUMINIUM(III)-DIPICOLINIC ACID IN AQUEOUS 0·5*M* SODIUM PERCHLORATE MEDIUM

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Summary—A potentiometric and spectrophotometric investigation on the formation of aluminium(III) complexes with dipicolinic (2,6-pyridinedicarboxylic) acid at 25° in aqueous 0·5*M* $NaClO_4$ medium is reported. The values of the cumulative formation constants of the two acid species HL^- and H_2L are $\log \beta_1 = 4{\cdot}532 \pm 0{\cdot}004$ and $\log \beta_2 = 6{\cdot}624 \pm 0{\cdot}006$. At pH < 4 and in the investigated concentration range ($0{\cdot}242 < C_M < 0{\cdot}975$ m*M*, $3{\cdot}16 < C_L < 5{\cdot}27$ m*M*), aluminium(III) forms two mononuclear complexes, one positively charged, with a metal/ligand molar ratio of 1:1, and the other negatively charged, with a metal/ligand molar ratio of 1:2. The two methods of investigation have yielded the following values for the cumulative formation constants:

$$\log \beta_{1(\mathrm{pot})} = 4{\cdot}87 \pm 0{\cdot}02; \quad \log \beta_{2(\mathrm{pot})} = 8{\cdot}32 \pm 0{\cdot}02$$
$$\log \beta_{1(\mathrm{sp})} = 4{\cdot}85 \pm 0{\cdot}03.$$

A precipitate occurs at pH 5–6. A paper electrophoretic investigation and comparison with the behaviour of the well-known iron(III) complexes, supports these findings.

AMONG the dicarboxylic acids of pyridine, dipicolinic acid (abbreviated hereafter as H_2L) seems to have the best chelating properties because it is terdentate. While the formation constants of complexes of several metal ions with this acid are well known,[1–6] we were unable to find any quantitative information about the aluminium(III)-dipicolinic acid system. The present work reports the results of an investigation of the various species existing in aqueous solution and of the formation constants of these at 25° in a constant ionic medium of 0·5*M* sodium perchlorate.

EXPERIMENTAL

Reagents

Dipicolinic acid (*Fluka*). The product was repeatedly recrystallized from water, dried at 115°, and checked by its melting point and spectrophotometric analysis; the dry acid was also checked by potentiometric titration against standard sodium hydroxide under a stream of pure nitrogen and appeared to be anhydrous. Therefore concentrated stock solutions were prepared by dissolving precisely weighed amounts of the anhydrous acid in suitably distilled water.

Aluminium perchlorate, $Al(ClO_4)_3{\cdot}8H_2O$ (*Rudi Pont*). Stock solutions, 0·01*M*, were prepared by dissolving the salt in water, avoiding any addition of acid, and taking care to use them as quickly as possible. They were standardized by complexometric titration with EDTA[7] and gravimetrically with 8-hydroxyquinoline.[8] Both these methods gave the same results to within 0·1%. Any free acidity was determined by titrating with sodium hydroxide the eluate obtained by percolating a known volume of solution through a cation-exchanger in the hydrogen form.[9] Within the experimental error of 0·1% the results did not show the presence of free acid.

Sodium hydroxide. A 0·1*M* solution was prepared by suitable dilution of a 50% w/w clear solution, and was then titrated potentiometrically against potassium hydrogen phthalate under a current of purified nitrogen.

Perchloric acid. A 0·1*M* solution was prepared by diluting pure 70% perchloric acid with distilled water and standardizing it with both sodium carbonate and hydroxide.

Sodium perchlorate, $NaClO_4 \cdot H_2O$. A 5*M* stock solution was prepared by dissolving the required weight of the salt in hot water, cooling, and making up to volume. The pH of the deaerated solution showed the absence of any free acid. The solution was standardized by hydrogen ion-exchange and subsequent titration.

In the more concentrated solutions of all reagents the absence of iron(III), chloride, sulphate and heavy metal ions was established by the most sensitive qualitative tests.

Apparatus

Potentiometer. Radiometer PHM 4c valve potentiometer with a Radiometer G202B glass electrode.

Spectrophotometers. Beckman DU and DK2A with 1-cm cells.

Procedure for potentiometric investigation

The e.m.f. measurements were performed at 25·0 ± 0·1° under a current of purified nitrogen passed through 0·5*M* sodium perchlorate solution, a Wilhelm cell being used as described by Forsling *et al.*[10]

$$\ominus \text{ glass electrode} \mid \text{test solution} \mid \text{reference} \oplus \qquad (1)$$

The reference half-cell was

$$\text{Ag, AgCl} \mid 0{\cdot}01M\ AgClO_4,\ 0{\cdot}49M\ NaClO_4 \mid 0{\cdot}50M\ NaClO_4.$$

The silver electrode was prepared as recommended by Brown.[11]

In a constant ionic medium the e.m.f. of the electrochemical cell (1) can be expressed, in the acid range, by

$$E = E_A{}^0 - 59{\cdot}16 \log [H^+]^* + E_{JA} \qquad (2)$$

in which $E_A{}^0$ is the formal potential of the cell and E_{JA} the liquid junction potential given by[12]

$$E_{JA} = J_A[H^+]. \qquad (3)$$

Similarly, in the alkaline range the e.m.f. (in mV) is:

$$E = E_B{}^0 + 59{\cdot}16 \log [OH^-] + E_{JB} \qquad (4)$$

$$= E_B{}^0 + 59{\cdot}16 \log [OH^-] + J_B[OH^-].$$

Since in the measurements used to calculate the constants of the aluminium(III)–dipicolinic acid system, the value 7 for $pc_H (= -\log [H^+])$ was never exceeded, adequate control of the glass electrode in the pc_H range between 2 and 7 was obtained by a series of measurements with the cell:

$$\ominus \text{ glass electrode} \mid \text{buffer solution, } 0{\cdot}5M\ ClO_4^- \mid H_2, \text{Pt} \oplus \qquad (5)$$

The e.m.f. of the cell given by (5) has been found to be constant within 0·1 mV, showing that the dependence of the e.m.f. of cell (1) on acidity of an acid medium is accurately described by equation (2) when the glass electrode is used.

Before and after each titration $E_A{}^0$ and J_A were determined by titrating a perchloric acid solution containing 0·5*M* perchlorate. It was also checked that the presence of aluminium(III) in the solution in the concentration range considered had no influence on the value of E_{JA}.

By using the glass electrode, $p(K_w)_c$ was also determined in the same ionic medium; a value of 13·73 was found, in agreement with the value reported by Lagestrom.[13]

In all the systems investigated in the present work, equilibrium was considered to be reached when two successive measurements yielded the same value of the potential within 0·1 mV; the results agreed with those obtained after the solutions had been standing for 2 days.

Method of calculation

The following equations can be written for each point of a titration curve of a dibasic acid H_2L, if complete dissociation of the added hydroxide and of the salts formed is assumed:

$$C_L = [H_2L] + [HL^-] + [L^{2-}] \qquad (6)$$

gives the mass balance for the acid, and

$$C_b + [H^+] = [OH^-] + [HL^-] + 2[L^{2-}] \qquad (7)$$

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* Here and later we shall not write the solvation water molecules for all the species considered.

is the electroneutrality condition when the added hydroxide is of the type M^+OH^-. C_L and C_b are respectively the analytical or total concentrations of the acid and of the added hydroxide.

The formation function of the acid, $\bar{n}_L$, is expressed as

$$\bar{n}_L = \frac{[HL^-] + 2[H_2L]}{[L^{2-}] + [HL^-] + [H_2L]} = \frac{\beta_{1L}[H^+] + 2\beta_{2L}[H^+]^2}{1 + \beta_{1L}[H^+] + \beta_{2L}[H^+]^2} \tag{8}$$

in which β_{1L} and β_{2L} are the cumulative formation constants of the acid species. From equations (6) and (7) the formation function can be expressed in terms of experimentally measurable quantities.

$$\bar{n}_L = \frac{2C_L - C_b - [H^+] + [OH^-]}{C_L} \tag{9}$$

In the presence of a metal ion bound to the ligand L (and present in a total concentration C_M) the total concentration of the acid is at each point of the titration curve given by

$$C_L = [H_2L] + [HL^-] + [L^{2-}] + \bar{n}C_M \tag{10}$$

where $\bar{n}$ is the formation function of the metal–ligand system.

As a first approximation, we can assume that both mixed complexes with hydrogen or hydroxide ions and hydrolytic products of the aluminium ion are negligible in comparison with the species Al_mL_n (the validity of this hypothesis has been checked, *vide infra*) so that

$$2C_L - C_b - [H^+] + [OH^-] = 2[H_2L] + [HL^-]. \tag{11}$$

From equations (8), (10) and (11) the formation function can be expressed in terms of experimentally measurable quantities

$$\bar{n} = \frac{C_L}{C_M} - \frac{2C_L - C_b - [H^+] + [OH^-]}{\bar{n}_L C_M}. \tag{12}$$

If the formation constants of the acid are substituted in equation (10), the concentration of the free ligand in solution can be obtained as

$$[L^{2-}] = (C_L - \bar{n}C_M)/(1 + \beta_{1L}[H^+] + \beta_{2L}[H^+]^2). \tag{13}$$

The constants of the acid and of the aluminium(III) complexes are calculated from the curves $\bar{n}_L(\log [H^+])$ and $\bar{n}(\log [L^{2-}])$, respectively, by a minimization method[14] using an IBM 7040 computer, starting from equation (8) and from the analogous equation

$$\bar{n} = \frac{\beta_1[L^{2-}] + 2\beta_2[L^{2-}]^2}{1 + \beta_1[L^{2-}] + \beta_2[L^{2-}]^2} \tag{14}$$

RESULTS

The titration curve of dipicolinic acid shows two equivalence points corresponding to the formation of the mono- and the disodium salt; in the measured pH range the protonated form H_3L^+ can be considered negligible in comparison with the other forms.[6] If aluminium(III) perchlorate is present in the acid solution in the concentration range $0{\cdot}242 < C_M < 0{\cdot}975$m*M*, which is less than the acid concentration ($3{\cdot}16 < C_L < 5{\cdot}27$m*M*)* in order to minimize any hydrolysis of the metal ion, there is a gradual splitting off of two protons per ion of aluminium(III) (after the first equivalence point of the acid) over the pH range 3·5–4. If the presence of hydrolytic and polynuclear species is negligible (see below), this means that the complexes AlL^+ and AlL_2^- are formed from HL^-. At pH > 4 the equilibrium is reached rather slowly which suggests that hydrolysis is appreciable. At pH 5–6 a white precipitate is observed.

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* The upper limit of this concentration range was chosen in order to avoid an appreciable change of the ionic strength of the solution, and the lower one in order to avoid too high experimental errors.

Figure 1 shows the formation function of dipicolinic acid, the values from which are used to calculate the formation constants of the acid under the experimental conditions, and Fig. 2 shows the formation function of the aluminium(III)–dipicolinic acid system. There is an irregular distribution of the calculated values in spite of the notable precision of the experimental data. This fact, already observed by others,[15,16] can be quantitatively treated for our system by comparing the standard deviation, σ, of the values before and after computation. For the calculated values of $\bar{n}$ the value obtained for σ was 0·05, and $\sigma = 0{\cdot}005$ was obtained for measured pc_H values referred to a fifth-order polynomial chosen on the basis of the number of the experimental points. The spread of the calculated points is such that it is not easy to consider these values as belonging to different curves; therefore, under these conditions, it can be assumed that polynuclear and hydrolytic complexes are not present in solution in any appreciable amount.

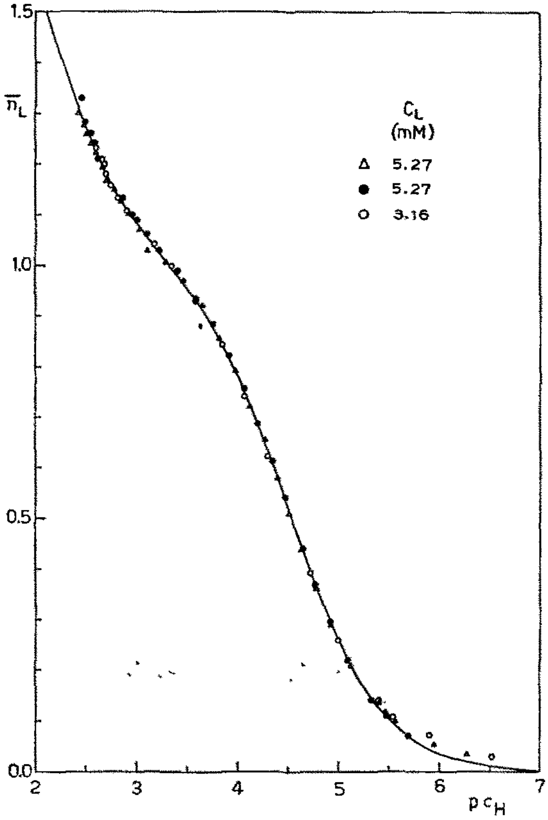

FIG. 1.—Formation function of dipicolinic acid.
Full curve calculated from the constants obtained in this work: $\log \beta_{1L} = 4{\cdot}532$, $\log \beta_{2L} = 6{\cdot}624$.

If we assume the formation of only two complexes AlL^+ and AlL_2^- and apply the graphical method described by Sillén,[17] we find that practically all the experimental points, excluding those corresponding to about $\bar{n} = 2$ ($pc_H > 4$), fall on the same normalized curve, in agreement with the previously mentioned hypothesis.

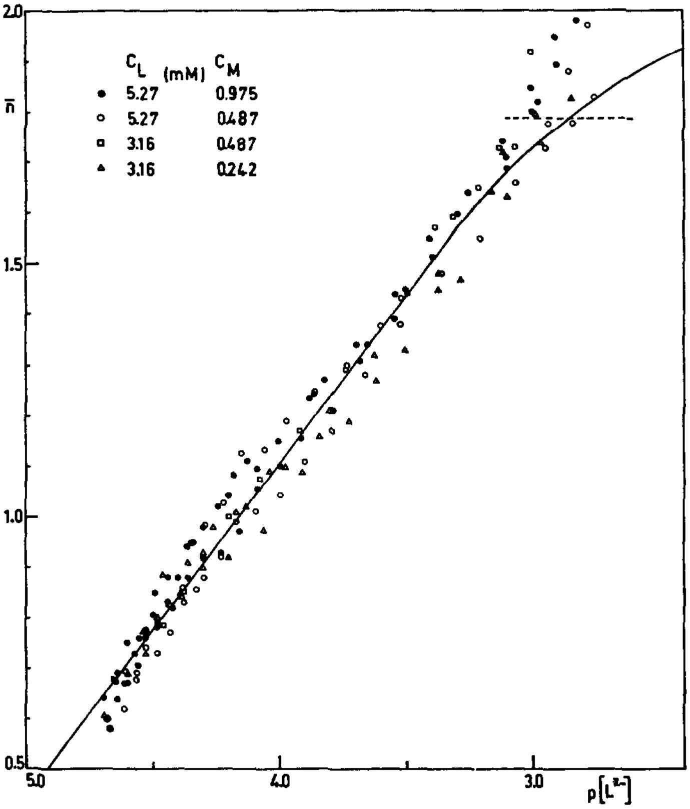

FIG. 2.—Formation function of aluminium(III)-dipicolinic acid system.
Full curve obtained from the constants calculated from potentiometric measurements:
$\log \beta_1 = 4{\cdot}87$, $\log \beta_2 = 8{\cdot}32$.

TABLE I.—CUMULATIVE FORMATION CONSTANTS OF DIPICOLINIC ACID AND OF ITS COMPLEXES WITH Al(III), OBTAINED AT 25° IN 0·5*M* $NaClO_4$.

$\log \beta_{1L}$	$4{\cdot}532 \pm 0{\cdot}004$
$\log \beta_{2L}$	$6{\cdot}624 \pm 0{\cdot}006$
$\log \beta_1$	$4{\cdot}87 \pm 0{\cdot}02$
$\log \beta_2$	$8{\cdot}32 \pm 0{\cdot}02$

Therefore, excluding the points above the dotted line in Fig. 2, the cumulative formation constants of the complexes were calculated by the method above.[14] Table I gives the cumulative formation constants of the acid and of the complexes with aluminium(III).

Equation (12) was deduced on the assumption that hydrolytic products of aluminium ions were negligible in comparison with the species AlL_n. The hydrolysis constant of aluminium(III) at 25° is[18]

$$K_t = \frac{[AlOH^{2+}][H^+]}{[Al^{3+}]} \simeq 10^{-5} \text{mole. l}^{-1}. \qquad (15)$$

and the formation constant of the complex AlL^+ is

$$\beta_1 = \frac{[AlL^+]}{[Al^{3+}][L^{2-}]} = 10^{4.87}\ l.\ mole^{-1}. \tag{16}$$

Division of equation (15) by equation (16) and introduction of the values of $[H^+]$ and $[L^{2-}]$ used in the calculations to give a minimum product gives

$$\frac{[AlOH^{2+}]}{[AlL^+]} = 0{\cdot}003.$$

Under such conditions the concentration of the hydrolysis products of the metal ion is certainly negligible in relation to the concentration of aluminium bound to L. Therefore all the approximations made in solving the equilibria from experimental data are admissible.

Procedure for spectrophotometric investigation

Dipicolinic acid shows a characteristic UV spectrum with a maximum at 272 mμ. The spectrum is modified by the addition of an aluminium(III) solution, with the formation of two absorption bands having maxima at 266 and 274 mμ and with an intermediate minimum at 270 mμ. Figure 3 shows the absorption spectra at pc_H 2 and 3–4, of the acid alone and of the acid plus a large excess of aluminium(III) ($C_L/C_M = 0{\cdot}016$), taken against a 0·5*M* perchlorate solution as a blank. These spectra are not modified if the solution is heated for 5 min at 80° and then cooled to 25°. Examination of these curves reveals the important fact that the complex with aluminium(III) has a lower molar absorptivity than the acid, so that it is practically impossible to study the system with sufficient accuracy in an excess of the ligand. This imposes a serious limitation, because it necessitates work with an excess of the metal, and therefore a low pH to minimize hydrolysis of the aluminium ion. Because the potentiometric investigation showed that complexes formed are not very stable, it was necessary to operate at as high a pH as possible, whilst ensuring a minimum concentration both of the undissociated ligand and of the metal ion hydrolysis products. pc_H 3·0 was chosen because at this value, according to our own potentiometric work and also other workers[17] the concentration of hydroxo-complexes is negligible with respect to the other forms of aluminium(III).

Figure 4 shows a differential spectrum of dipicolinic acid recorded at pc_H 3·0 against a solution of acid having the same concentration but containing a large excess of aluminium(III). While the maximum of ΔA at 262 mμ gives values too low to be used for quantitative purposes, the ones at 270 and 280 mμ can be used.

Because at pc_H 3·0 and in the concentration range of aluminium(III) and of total ligand examined the ratio of the ΔA values at the characteristic wavelengths remains constant with varying C_L/C_M, it can be assumed that only one complex is of importance.

Job's method of equimolar solutions[19] was applied to obtain some indications about the composition of the complex in solution at pc_H 3·0. The results are shown in Fig. 5, the maximum at 0·5 molar fraction showing that a complex Al_mL_n with $m = n$ is predominant.

The "straight-line" method[20–23] was used to establish the presence or absence of a mononuclear complex. The results used are given in Table II, in which the absorbance values are the means of three measurements which agreed within 1%. By the modified method of calculation adopted in our Institute,[23] the value $m = 1$ can be obtained, and since $m = n$ as explained above, a 1:1 metal: ligand molar ratio can be deduced for the complex. In this case the calculation of the conditional formation constant,[24] gives a mean value of $(1{\cdot}8 \pm 0{\cdot}1) \times 10^3$ l. mole^{-1}.

As explained above, it is impossible to detect the presence of the 1:2 complex spectrophotometrically.

DISCUSSION

In the examined range of concentrations and at pH < 4, aluminium(III) gives two mononuclear complexes with dipicolinic acid, with metal:ligand molar ratios of 1:1 (AlL^+) and 1:2 (AlL_2^-).

The formation constants obtained by spectrophotometry and potentiometry can be compared by converting the conditional formation constant (β_1') determined at

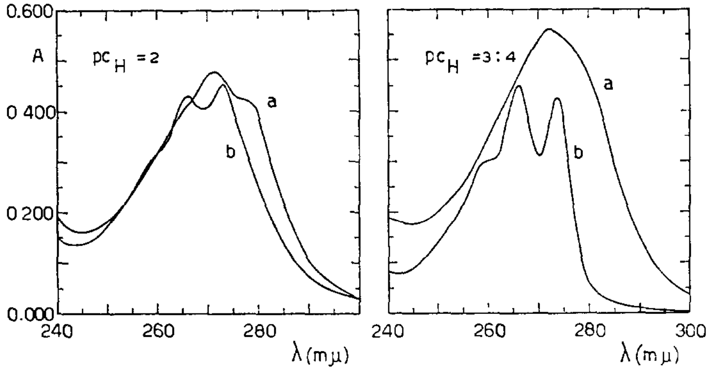

Fig. 3.—Absorption spectra of the aluminium(III)–dipicolinic acid system at 25°C in 0·5*M* NaClO$_4$ (1-cm cells).
Curve *a*: acid alone, $C_L = 8 \times 10^{-5} M$.
Curve *b*: acid plus aluminium(III); $C_L = 8 \times 10^{-5} M$, $C_M = 5 \times 10^{-3} M$.
Reference: 0·5*M* NaClO$_4$.

Table II.—Data used to calculate β_1' by the "straight-line" method[20–22]

$1{\cdot}00 \times 10^{-2} M$ metal added, *ml*	*A*, 270 *mμ*	*A*, 280 *mμ*
—	0·552	0·475
1·00	0·482	0·352
2·00	0·440	0·280
4·00	0·395	0·195
8·00	0·358	0·127
16·00	0·330	0·075

$C_L = 8{\cdot}00 \times 10^{-5} M$; total volume 50 ml; temperature 25°; 0·5*M* NaClO$_4$ medium.

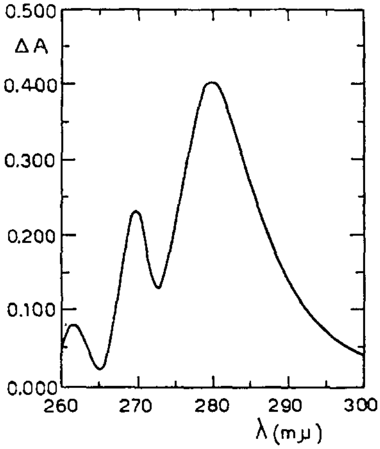

Fig. 4.—Absorption spectrum of dipicolinic acid ($C_L = 8 \times 10^{-5} M$) recorded against a solution of acid plus aluminium(III).
($C_L = 8 \times 10^{-5} M$, $C_M = 5 \times 10^{-3} M$) in 0·5*M* NaClO$_4$
$T = 25$°C, pc$_H$ = 3·0, 1-cm cells.

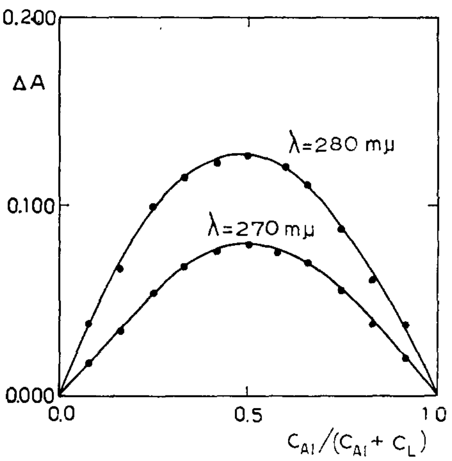

FIG. 5.—Job's method of equimolar solutions. $C_{Al} + C_L = 2{\cdot}4 \times 10^{-4}M$, $T = 25°C$, $pc_H = 3{\cdot}0$, $0{\cdot}5M$ $NaClO_4$, 1-cm cells.

$pc_H = 3{\cdot}0$ into the formation constant (β_1) by means of the protolytic side-reaction coefficient.[24] The formation constant is related to the conditional one by the expression

$$\beta_1 = \beta_1' \cdot \alpha_{Al}\alpha_L/\alpha_{AlL}. \tag{17}$$

In this case

$$\alpha_{Al} = 1 + K_i/[H^+]$$
$$\alpha_L = 1 + \beta_{1L}[H^+] + \beta_{2L}[H^+]^2$$
$$\alpha_{AlL} = 1 \text{ (deduced from the potentiometric results)}$$

β_{1L} and β_{2L} are the formation constants of the acid, and K_i is the hydrolysis constant of the metal ion. At pc_H 3·0, $\alpha_{Al} = 1{\cdot}01$,[18] and $\alpha_L = 39{\cdot}3$ are obtained. The introduction of numerical values into equation (17) gives

$$\beta_1 = (7{\cdot}1 \pm 0{\cdot}4) \times 10^4 \text{ l. mole}^{-1}$$
$$\log \beta_1 = 4{\cdot}85 \pm 0{\cdot}03$$

in good agreement with the potentiometric results.

Figure 6 shows the distribution curve referring to the two complexes we found to

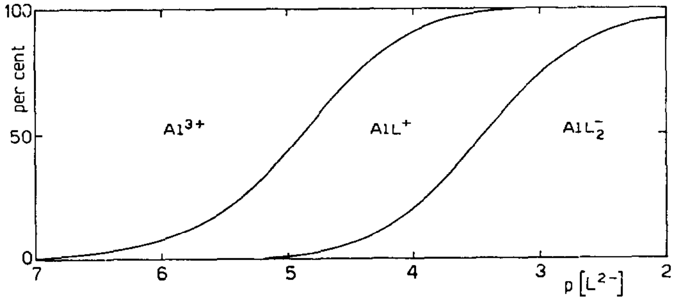

FIG. 6.—Distribution diagram for aluminium(III)-dipicolinic acid complexes, using the constants calculated from potentiometric measurements ($\log \beta_1 = 4{\cdot}87$, $\log \beta_2 = 8{\cdot}32$).

be formed under our conditions between aluminium(III) and dipicolinic acid. At pc_H 3·0, for a total acid concentration of about 10^{-4} *M*, as used for the spectrophotometric measurements, the free ligand concentration (C_L/α_L) is 2×10^{-6} *M*, and therefore $p[L^{2-}] = 5{\cdot}7$. From the distribution curve it can be seen how, for such a concentration of free ligand, the concentration of AlL_2^- is negligible as compared with those of AlL^+ and Al^{3+}. The effect of aluminium(III) is merely displacement of $p[L^{2-}]$ toward higher values, and therefore it acts against the formation of the 1:2 complex. These considerations agree with the results of the spectrophotometric investigation.

The results obtained were further confirmed by a paper electrophoretic comparative investigation of the behaviour of iron(III), the formation constants of complexes formed between this ion and the considered ligand being known.[4] The results (Table III) confirm that bonding between aluminium(III) and dipicolinic acid takes place at pH values as low as ~2. Cationic species are seen to predominate up to pH 3, and anionic species at pH 4. In the considered pH range iron(III) forms an anionic complex, in agreement with the results obtained by Anderegg.[4] It can be concluded that by using dipicolinic acid as the complexing agent, iron(III) and aluminium(III) can be successfully separated by paper electrophoresis and probably also by ion-exchange, providing that the working pH is maintained between 2 and 3.

TABLE III.—PAPER ELECTROPHORESIS OF Al(III) AND Fe(III) IN 0·1*M* $NaNO_3$ ($+HNO_3$) AND 0·1*M* $NaNO_3$ + 10^{-2}*M* H_2L ($+HNO_3$ OR NaOH) SOLUTIONS

pH	Distance run by Al(III), *mm*		Distance run by Fe(III), *mm*	
	$NaNO_3$	$NaNO_3 + H_2L$	$NaNO_3$	$NaNO_3 + H_2L$
2	+52	+28	+45	−15
3	+46	+6	0	−18
4	+50	−10	0	−18
5	+51	−10	0	−17

Voltage 100 V d.c.; temperature 25°; time 2 hr; Schleicher and Schüll paper 2043b, 30 × 2 cm; + = cation; − = anion.

Acknowledgements—The author wishes to express his gratitude to Prof. G. De Angelis for his interest and helpful discussions. The work was carried out with aid from CNR.

Zusammenfassung—Eine potentiometrische und spektrophotometrische Untersuchung der Bildung von Aluminium(III)-Komplexen mit Dipicolinsäure (Pyridin-2,6-dicarbonsäure) bei 25° in wäßrigem 0,5 M Na^+/ClO_4^--Medium wird mitgeteilt. Die Werte der kumulativen Bildungskonstanten der beiden Säurespezies HL^- und H_2L sind $\log \beta_1 = 4{,}532 \pm 0{,}004$ und $\log \beta_2 = 6{,}624 \pm 0{,}006$. Bei pH 4 und im untersuchten Konzentrationsbereich ($0{,}242 < c_M < 0{,}975$ mM, $3{,}16 < c_L < 5{,}27$ mM) bildet Aluminium(III) zwei einkernige Komplexe, von denen der eine positiv geladen mit einem Metall-Ligand-Verhältnis 1:1 ist, der andere negativ geladen mit dem Verhältnis 1:2. Die beiden Untersuchungsmethoden lieferten für die kumulativen Bildungskonstanten folgende Werte:

$$\log \beta_{1(\text{pot})} = 4{,}87 \pm 0{,}02 \qquad \log \beta_{2(\text{pot})} = 8{,}32 \pm 0{,}02.$$
$$\log \beta_{1(\text{sp})} = 4{,}85 \pm 0{,}03$$

Bei pH 5–6 fällt ein Niederschlag aus. Eine papierelektrophoretische Untersuchung und Vergleich mit dem Verhalten der wohlbekannten Eisen(III)-Komplexe untermauert diese Feststellungen.

Résumé—On décrit une recherche potentiométrique et spectrophotométrique sur la formation de complexes de l'aluminium(III) avec l'acide dipicolinique (2,6-pyridinedicarboxylique) à 25° en milieu 0,5*M* $Na^+ClO_4^-$. Les valeurs des constantes de formation cumulatives des deux espèces acides HL^- et H_2L sont: $\log \beta_1 = 4{,}532 \pm 0{,}004$ et $\log \beta_2 = 6{,}624 \pm 0{,}006$. A pH 4 et dans le domaine de concentration étudié ($0{,}242 < C_M < 0{,}975$ m*M*, $3{,}16 < C_L < 5{,}27$ m*M*), l'aluminium(III) forme deux complexes mononucléaires, l'un chargé positivement avec un rapport molaire métal/ligand de 1:1 et l'autre chargé négativement, avec un rapport molaire métal/ligand de 1:2. Les deux méthodes d'étude ont donné les valeurs suivantes pour les constantes de formation cumulatives:

$$\log \beta_{1(\mathrm{pot})} = 4{,}87 \pm 0{,}02; \quad \log \beta_{2(\mathrm{pot})} = 8{,}32 \pm 0{,}02$$
$$\log \beta_{1(\mathrm{sp})} = 4{,}85 \pm 0{,}03$$

Un précipité se forme à pH 5–6. Une étude par électrophorèse sur papier et une comparaison avec les comportement des complexes bien connus du fer(III) viennent à l'appui de ces résultats.

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SPECTROSCOPY IN SEPARATED FLAMES—II

THE USE OF THE SEPARATED AIR–ACETYLENE FLAME IN LONG PATH ATOMIC ABSORPTION SPECTROSCOPY

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Summary—The application of a separated air–acetylene flame to the determination of several elements by long-path atomic-absorption spectroscopy is described. The factors which govern the stability and reproducibility of the separated flame have been investigated. High sensitivity and stability and low background absorption are obtained in the the determination of zinc, iron, copper, mercury, magnesium and silver by the method described.

The use of the separated air–acetylene flame in thermal emission spectroscopy, for which it has the advantages of very low background emission and high stability, has already been described.[1] As part of a study of the general utility of separated flames in analytical flame spectroscopy we became interested in the possible use of the separated air–acetylene flame in atomic-absorption spectrophotometry. Our initial investigation made use of the same burner arrangement as that described for emission spectroscopy. The determination of iron by atomic-absorption spectrophotometry with this system was found, as expected, to be relatively insensitive owing to the short path length. The results, however, revealed that the absorbance due to iron decreased much less rapidly along the vertical axes of the separated flame than of the unseparated flame. This is probably due to the maintenance of a more reducing atmosphere of uncombusted carbon monoxide and hydrogen higher in the separated than in an unseparated premixed flame. The background absorption from the flame gases was also lower between 2600 and 3250 Å where strong OH absorption is encountered in normal flames. We decided from these results that the separated flame might have several advantages in atomic-absorption spectroscopy, provided that a sufficiently long path-length through the flame could be obtained. This paper describes apparatus constructed to obtain a long absorption path-length in the separated air–acetylene flame, and the results obtained with it for the determination of zinc, mercury, copper, silver, magnesium and iron.

EXPERIMENTAL

Apparatus

Techtron AA4 atomic-absorption spectrophotometer and SRL Sargent recorder. Brass hollow-cathode lamp (Hilger & Watts) for zinc and copper and high-intensity hollow-cathode lamps for iron and silver (Atomic Spectral Lamps Pty. Ltd.). Standard hollow-cathode lamp for magnesium. A mercury electrodeless discharge tube similar to those previously described[2] was used for the determination of mercury. This tube was constructed of clear quartz tubing (8 mm i.d., 95 mm long). Triply distilled mercury (0·4 g) was placed in the tube, and the tube was sealed at an argon filler-gas pressure of 0·04 mm Hg. The tube ends were contained in a small electrically heated oven. This serves to warm the tube before the discharge is initiated and to stabilize the tube temperature during subsequent operation of the source. The cavity was cooled with air supplied from a small compressor. Excitation was obtained at 2450 Mc/s from a microwave generator (Electromedical Supplies

Ltd., Microtron 200) fitted with a 214L cavity. The tube was operated at a setting corresponding to a power of 10 W. Twenty min were required for the tube output intensity to become stable within ±2%/hr, and no serious deterioration in performance was observed after 60 hr.

Long-path separated flame. The apparatus constructed is shown in Fig. 1. A Unicam air–acetylene emission burner head was attached to the Pyrex flame separator head with an asbestos sealing ring. The Pyrex separator head consists of a tube of diameter 21 mm and length 110 mm. A side-arm of 15-mm dia. tubing was sealed to this head 57 mm above the base as shown. A B14 ground-glass cone was joined optically in line with the side-arm on the opposite side of the head. A silica window (15 mm dia.) attached to a B14 ground-glass socket was fitted to the cone to provide a transparent window. In order to increase the flexibility of the system, a third side-arm (6 mm i.d.) was incorporated into the separator head in line with the B14 cone but 15 mm above it. Hydrogen is supplied through this side-arm to stabilize the separated flame when fuel-lean mixtures are used. As shown in Fig. 1, the side-arm was joined to a translucent silica tube (12 mm i.d., length 270 mm) *via* an asbestos gasket and Pyrex glass sleeve. A similar asbestos seal and Pyrex sleeve were used to attach a Pyrex tube (15 mm i.d., length 50 mm) to the opposite end of the long silica tube. A ground-glass cone on this tube supports a B19 ground-glass socket to which is fitted a fused silica window (19 mm dia.). The Pyrex exhaust tube shown in Fig. 1 was fitted 20 mm from the end of the long silica tube. This exhaust tube was attached to the extraction duct of the exhaust hood of the apparatus in order to draw the flame gases through the system.

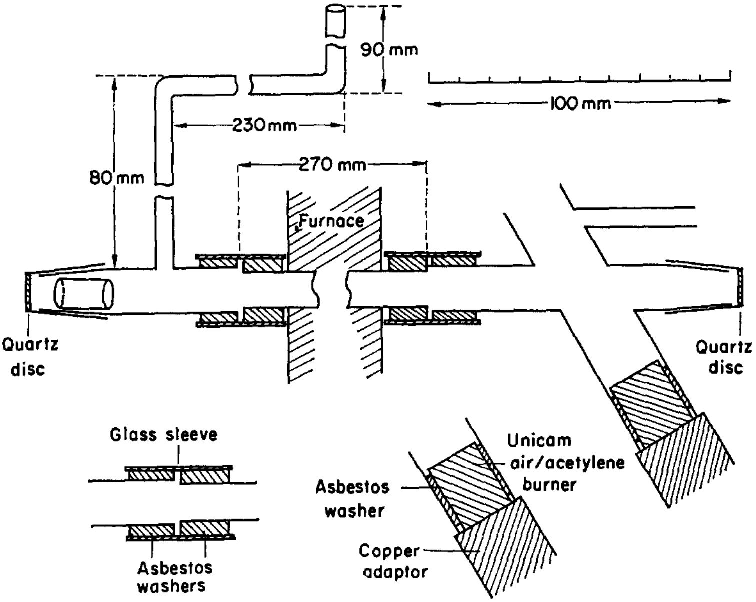

FIG. 1.—Diagram of long-path burner.

A micro-analytical furnace, 25-cm long, with a high temperature winding (Kalthin) operated from a Variac transformer was placed round the quartz tube to provide auxiliary heating to 1100°. A platinum–iridium thermocouple was placed at the centre of the furnace beside the silica tube to monitor the temperature. The burner head was attached to the Techtron indirect nebulizer *via* a copper adaptor. Aspiration *via* this nebulizer was by air, pressure 15 lb/in^2, and both air and acetylene were supplied from the Techtron gas control unit.

Reagents

Analytical reagent grade materials were used throughout. Metal ion solutions were prepared by dilution of 1000 ppm solutions of their simple salts.

RESULTS AND DISCUSSION

Flame characteristics

Stable separated flames are obtained over a range of air and acetylene mixture strengths comparable to those reported for the stability limits of the simple separated flame.[1] Stoichiometric and fuel-rich flames can be separated and stabilized without any auxiliary hydrogen supply to the top of the glass separator. Very fuel-lean flames, however, require that hydrogen be provided above the primary zone in order to retain the separated secondary zone at the upper edge of the Pyrex separator. The gases from the interconal zone of the air–acetylene flame are drawn down the side-arm and through the long quartz tube by the Techtron fan extraction system. The use of excessively high hydrogen flow-rates to support very lean flames leads to dilution of the gases in the side-arm by hydrogen, and a corresponding decrease in absorbance for elements introduced into the flame.

Absorption from elements in the flame

The elements investigated in this study were copper, zinc, magnesium, mercury, silver and iron. The effect of furnace temperature and fuel flow-rate on the sensitivity obtained for these elements was investigated. The precision of their determination and the effect of different anions was also studied.

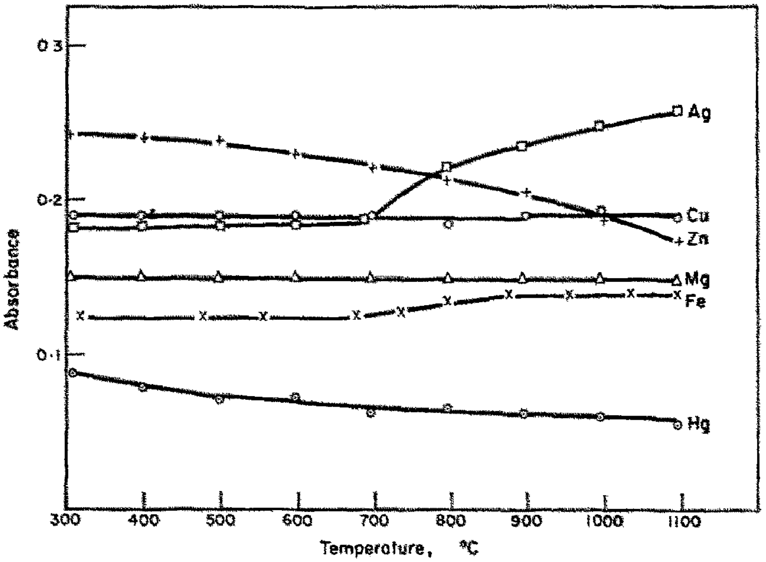

FIG. 2.—Effect of furnace temperature on absorbance.

Effect of furnace temperature. The effect of variation in furnace temperature at fixed air–acetylene–hydrogen flow-rates and metal ion solution concentrations was investigated. The results of this study are shown in Fig. 2. It is evident that over the range studied the side-arm furnace temperature has in general little effect on the absorbance obtained in the long-path flame for the elements investigated. The decrease in absorbance with increase in temperature for mercury and zinc may be explained by consideration of the volume of the partly combusted gas mixture. Mercury and zinc have a sufficiently high vapour pressure at the lower temperatures to ensure a high population of ground state atoms. Increase in temperature expands the gas mixture, and this "dilution" effect in the light path outweighs any increase in atomic concentration caused by the higher temperature. It appears that for silver, copper, iron and magnesium, however, which are relatively involatile, the "dilution" effect caused by expansion is outweighed at higher temperatures by the more efficient maintenance of the atom population.

The furnace serves to maintain high temperatures throughout the length of the silica tube, but does not radically alter the absorbance gradient which exists in the tube without the furnace in operation. Use of the furnace, however, does allow selection of the optimum conditions for maximum sensitivity for different elements.

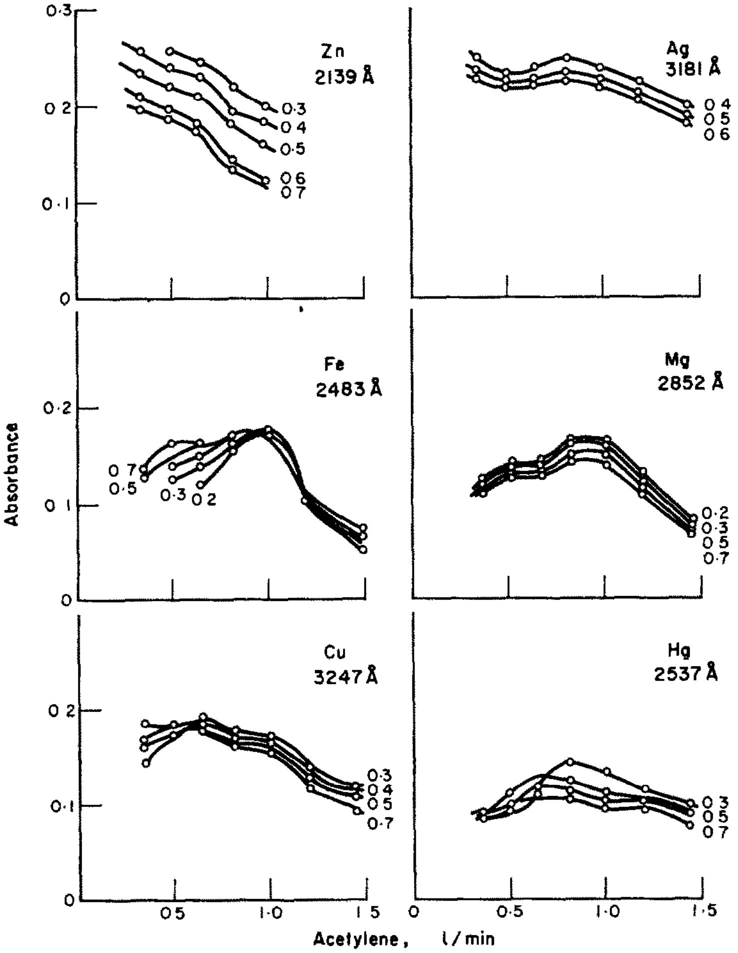

FIG. 3.—Effect of acetylene flow-rate (l/min) on absorbance at different hydrogen flow-rates (l/min).

Effect of fuel flow-rate

The effect of acetylene flow-rate on the absorbance produced by the elements investigated was studied under the optimum furnace temperature conditions. The air supplied *via* the nebulizer was maintained at a constant pressure of 15 lb/in^2, and the effect of acetylene flow-rate on absorbance was studied at different auxiliary hydrogen flow-rates. The results obtained are shown in Fig. 3. These show that there is an optimum acetylene flow-rate for each element, and that at high auxiliary hydrogen flow-rates a dilution of the side-arm gases by hydrogen occurs. The minimum acetylene flow-rate, beyond which it is not possible to maintain a separated flame without an auxiliary supply of hydrogen, is 1·2 l/min.

Sensitivity and precision. Figure 4 shows the absorbance growth curves under conditions for the elements examined. As expected, it is the more volatile elements which show the greatest increase in sensitivity with this apparatus over the sensitivity obtained in a normal flame. The absolute sensitivities are considerably better than those obtained with commercially available atomic-absorption burners. Table I shows a comparison of the absolute sensitivities obtained for the elements examined with our apparatus with those obtained by other workers. Fuwa and Vallee[3] and Koirtyohann *et al.*[4,5] have utilized 91 and 40-cm Vycor tubes respectively. Ramakrishna *et al.*[6] have described a 15-cm T-piece adaptor, and McGee and Winefordner[7] have used a 12-in. flame cell and a continuum source of radiation. The flames which these workers have examined are oxy-hydrogen,[4–6] air–hydrogen[3] and argon–hydrogen–entrained air.[7] Each of the long-path systems previously reported has utilized total-consumption

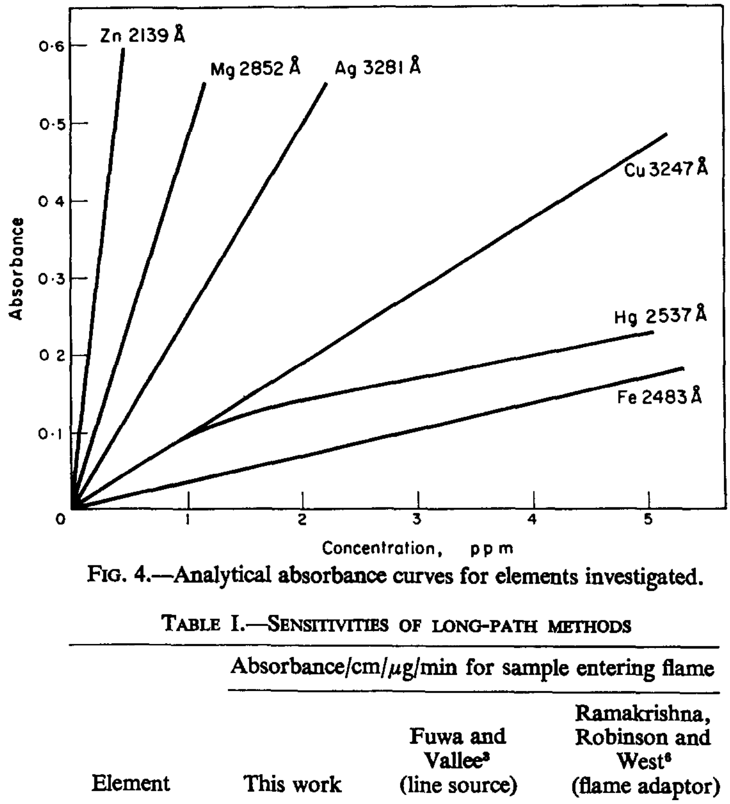

FIG. 4.—Analytical absorbance curves for elements investigated.

TABLE I.—SENSITIVITIES OF LONG-PATH METHODS

	Absorbance/cm/μg/min for sample entering flame		
Element	This work	Fuwa and Vallee[3] (line source)	Ramakrishna, Robinson and West[6] (flame adaptor)
Ag 3281 Å	0·011	—	—
Cu 3247 Å	0·004	0·004	0·009
Fe 2483 Å	0·0015	—	—
Hg 2537 Å	0·05	—	—
Mg 2852 Å	0·02	0·006	—
Zn 2139 Å	0·07	0·05	0·036

atomizer-burners which produce turbulent flames. It is our experience that in such flames, when acetylene is used as fuel, poor precision arises from high background absorbance and the deposition of carbon on windows and lenses. The results shown reveal that the sensitivities we obtain compare favourably with those obtained in the extended path systems previously reported. The high atomization efficiency probably results from the increased residence time of the atoms in the system and the absence of the secondary oxidizing mantle of the normal premixed flame.

The background absorption of the flame plasma in the separated flame is much lower than in a conventional flame, particularly between *ca.* 2800 and 3300 Å where strong absorption from the OH radical would normally be exhibited. The most intense heads of the ultraviolet bands of OH occur at 2811 Å (1, 0) and 3064 Å (0, 0). This lower background absorption results in higher sensitivity, particularly for silver (3281 Å), magnesium (2852 Å) and copper (3247 Å). A similar explanation based on the low background of the argon–hydrogen–entrained air flame has been proposed by Winefordner and McGee[7] to explain in part the high sensitivities obtained by them with this flame. Owing to the low background absorption and the very high stability of our arrangement utilizing the separated flame, we have been able to obtain high reproducibility for the determination of the elements examined. The precision of the determinations was established by measurement of a solution of each element nine times. The concentration of each element was chosen to produce an absorbance in the middle of the working range of its calibration curve (*i.e.*, *ca* 0·2 absorbance unit). The relative standard deviations in the absorbances produced were magnesium 0·8%, zinc 0·7%, copper 0·7%, mercury 2·7%, silver 0·5% and iron 0·6%. The relatively poor precision for mercury is not due to instability of the electrodeless discharge source used, and may be accounted for by the specific observations on the determination of mercury described below.

Effect of common anions

The determination by atomic-absorption spectroscopy of the elements investigated with our apparatus is free, as expected, from interference by a wide range of cations. No interference is experienced from the presence of 100 to 1000-fold excesses by weight of the anions sulphate, nitrate, chloride and acetate. The presence of very large excesses (10^4- or 10^5-fold by weight) of these ions, however, may cause serious interference for some elements. Table II shows the effect of high concentrations of mineral acids on the absorbance produced by the elements investigated. Provided that the matrix composition is known approximately when a trace constituent is to be determined, it is a relatively simple matter to correct for the anionic interference by preparation of blank solutions and sample solutions of approximately the same composition.

Determination of mercury

The calibration curve for mercury shown in Fig. 4 was obtained by using a dilute mercury(II) nitrate solution. The sensitivity is four times as great for mercury(I) as for mercury(II). This is not a property specific to our experimental arrangement and has also been observed in normal unseparated premixed flames.[8,9] Preliminary studies to investigate this effect have revealed that the addition of excess of tin(II) chloride or ascorbic acid to mercury solutions before aspiration produces as much as a 20-fold increase in absorbance, *i.e.*, a further 5-fold enhancement of the sensitivity. It seems probable that the atomization efficiency in the flame is improved by presentation of the mercury as the colloidal reduced element in this way. The increases in sensitivity obtained in the presence of reductants are reproducible, although the reduced mercury solutions are not stable for more than 10 min. If reductants are added to increase sensitivity, a rigid schedule between addition of the reducing agent and measurement must, therefore, be adhered to.

TABLE II.—EFFECT OF HIGH CONCENTRATIONS OF ACIDS ON ABSORBANCE

Absorbances for:	Cu 2 ppm	Ag 0·6 ppm	Hg 5 ppm	Mg 0·5 ppm	Zn 0·15 ppm	Fe 4 ppm
Distilled water	0·190	0·145	0·215	0·24	0·25	0·13
10% H_2SO_4	0·01	0·100	0·194	0·22	0·15	0·06
10% CH_3COOH	0·190	0·163	0·38	0·29	0·25	0·12
10% HNO_3	0·155	0·143	0·13	0·25	0·22	0·06
10% HCl	0·174	0·165	0·108	0·25	0·19	0·11

CONCLUSIONS

Other workers[3,4,7] have already demonstrated the utility of long-path flame cells in atomic-absorption spectroscopy for the determination of a range of elements. The apparatus we have developed, based on the separated air–acetylene flame, has several other advantages as well as that of the high sensitivity shown by long-path cells previously described. The use of a premixed flame and indirect nebulizer results in high precision and flame stability. It is our experience that although absolute sensitivity is lower with this nebulizer system than with a total-consumption atomizer-burner, the presence of large droplets of solution in the turbulent flame from the latter burner leads to higher background and noise levels. The use of a premixed flame into which a fine mist is introduced may also explain why we have found less serious anion interference with our apparatus than that reported for the turbulent burner system.[5] The use of the separated-flame premixed burner system also makes possible the use of air–hydrocarbon flames in the long tube without significant loss of signal or sooting-up, and facilitates the maintenance of a reducing atmosphere in the tube. It is also our opinion that the gas flow in the long tube is more laminar in nature than the flow obtainable from a burner producing a turbulent flame which entrains some air. The flow pattern in the tube undoubtedly has a pronounced effect on the sensitivity, precision and noise levels obtained.

Acknowledgement—We are grateful to Murex Ltd. (Rainham, Essex) for the provision of equipment, and for granting study leave to one of us (D. N. H.).

Zusammenfassung—Die Verwendung einer aufgetrennten Luft-Acetylen-Flamme zur Bestimmung mehrerer Elemente durch Atomabsorptionsspektrometrie bei größer optischer Weglänge wird beschrieben. Die Stabilität und Reproduzierbarkeit der aufgetrennten Flamme beeinflussenden Faktoren wurden untersucht. Bei der Bestimmung von Zink, Eisen, Kupfer, Quecksilber, Magnesium und Silber mit der beschriebenen Methode erzielt man hohe Empfindlichkeit und Stabilität sowie niedrige Untergrundabsorption.

Résumé—On décrit l'application d'une flamme séparée air-acétylène au dosage de plusieurs éléments par spectroscopie d'absorption atomique à longue marche. On a étudié les facteurs gouvernant la stabilité et la reproductibilité de la flamme séparée. Par la méthode décrite, on obtient de hautes sensibilité et stabilité, et une faible absorption de fond dans les dosages des zinc, fer, cuivre, mercure, magnésium et argent.

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ESTIMATION OF MINIMUM DETECTABLE SAMPLE CONCENTRATIONS OBTAINED WITH NEAR AND MIDDLE INFRARED DETECTORS FOR INFRARED ABSORPTION SPECTROPHOTOMETRY

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Summary—An expression is given to allow estimation of the minimum detectable sample concentration of a molecular absorber measured by any infrared spectrophotometer using photon or thermal detectors. Typical plots are given of minimum detectable sample concentration *vs.* wavelength for a hypothetical absorber with a molar absorptivity of unity and for several different photon and thermal detectors. Such plots, used along with the general expression, are useful for selecting the optimum detector for a given infrared measurement and for estimation of the minimum detectable sample concentration measured by a specific spectrometric system.

THE minimum detectable sample concentration C_{mp} in absorption spectrophotometry is normally defined as that concentration resulting in a fixed minimal detectable absorbance, $A_{\min}$ namely

$$C_{mp} = \frac{A_{\min}}{\varepsilon_\lambda b}. \tag{1}$$

where ε_λ is the molar absorptivity at the wavelength of measurement, λ, and b is the sample cell thickness in the direction of the incident radiation. The value of $A_{\min}$ is normally taken to be about 0·002 for ultraviolet or visible absorption spectrophotometry of substances in the condensed phase when a photomultiplier detector is used, and to be about 0·02 for infrared absorption spectrophotometry for substances in the condensed phase, when infrared detection devices are used.

In many instances,[1] experimental conditions may be such that the minimum detectable sample concentration in absorption spectrophotometry is limited by the signal-to-noise ratio, and in this case, the minimum detectable sample concentration, C_{mt}, is defined[2] as that concentration resulting in a signal-to-noise ratio, $(V_B - V_S)/V_N$, given by

$$\frac{V_B - V_S}{V_N} = \frac{t\sqrt{2}}{\sqrt{n}} \tag{2}$$

where V_B is the detection signal, in V, due to radiation from the light source passing through the blank solution and falling on the detector surface, V_S is similarly defined for radiation which has barely been attenuated by passing through the sample solution

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containing the minimum detectable sample concentration, V_N is the total root-mean-square noise signal, in V, due to all sources of noise, and t is the "Student" t which is found in statistical tables for a given confidence level, *e.g.*, 99·5%, and a given number of degrees of freedom, *i.e.*, $2n-2$, where n is the number of pairs of sample and blank measurements. If n equals 6 at a 99·5% confidence level, $t\sqrt{2}/\sqrt{n}$ is approx 2·0 (a commonly used value of $(V_B - V_S)/V_N$ at the minimum detectable sample concentration). This latter method of determining C_{mt} is valid if random and systematic errors such as sampling errors (including fingerprints, dust, blemishes, *etc.*, on the cell surface, and unknown absorbing impurities in the solution), cell-positioning errors from sample to sample, errors due to variation in cell path-length from sample to sample, and erratic photodetector behaviour (including fatigue) are absent, minimized, or accounted for. If such errors are present, the analyst may obtain a more reliable value of the minimum detectable sample concentration if a reliable estimate of $A_{\min}$ is chosen, and equation (1) is used. Unfortunately, a reliable estimate of $A_{\min}$ depends on the kind of substance measured and on the type and state of each instrumental component used in the absorption spectrophotometer, as well as on the combination of instrumental components, and therefore it is difficult to estimate a value of $A_{\min}$ without resorting to experimental measurements of signal-to-noise ratios at various sample concentrations. Therefore equation (2) is more useful in estimating minimum detectable sample concentrations prior to any experimental work. Perhaps the most significant aspect of this approach is in determining the applicability of infra-red spectrophotometry to qualitative identification of certain infrared bands of molecules in various systems. For example, it may be found that for minimum detectability of a given infrared vibration, an inordinately large amount of sample is needed for the instrumental system used.

A parameter (sometimes called figure of merit) important to the study of thermal detectors,[3–6] *e.g.*, bolometer, thermocouple, thermopile, Golay, is the detectivity, D^*, in cm $W^{-1}sec^{-1/2}$. A parameter important to the study of photon detectors,[3–6] *e.g.*, photoemissive, photoconductivity, photovoltaic, and photoelectromagnetic detectors is the spectral detectivity, D_λ^*, in cm W^{-1} $sec^{-1/2}$. Values of the detectivity and spectral detectivity are often cited in manufacturers' literature along with other detector specifications. The parameters D^* or D_λ^* (see Appendix for discussion of the interrelationship between D_λ^* and γ, the photoanodic sensitivity) is defined by

$$D_\lambda^* = \frac{\sqrt{A_D}}{P_N} = \frac{\sqrt{(\Delta f A_D)}}{P}\frac{V}{V_N}, \tag{3}$$

where P_N is the noise equivalent power of a detector, in W $sec^{-1/2}$, and is also a figure of merit, P is the root-mean-square (r.m.s.) value of the incident power, in W, A_D is the area of the detector surface illuminated by radiation, in cm^2, and V/V_N is the ratio of the r.m.s. signal voltage due to radiation striking the detector, to the r.m.s. noise voltage (if a d.c. voltage is being measured, V is then the d.c. voltage; otherwise V is $1/2\sqrt{2}$ of the peak value of the voltage signal). In equation (3) it has been implicitly assumed that Δf is chosen sufficiently small for the noise voltage per cycle within Δf to be independent of f_0, the chopping frequency. The major source of noise in photon infrared detectors is usually noise due to the detector itself whereas in thermal infrared detectors the major sources of noise are the detector and photon sources. Other noises such as amplifier-readout noise are generally negligible.

Another figure of merit of infrared detectors is the responsivity, R_λ(VW^{-1}), which is defined by

$$R_\lambda = V/P. \tag{4}$$

The responsivity can also be written in terms of the r.m.s. noise voltage, V_N, by use of equations (3) and (4):

$$R_\lambda = V_N D_\lambda^* / \sqrt{(A_D \Delta F)}\,. \tag{5}$$

At the minimum detectable sample concentration,[1] C_{mt}, the detector must distinguish between the r.m.s. power of radiation transmitted by the blank, P_B, and that transmitted by the sample, P_S, and so

$$(V_B - V_S) = R_\lambda(P_B - P_S) \tag{6}$$

and therefore

$$\frac{V_B - V_S}{V_N} = \frac{t\sqrt{2}}{\sqrt{n}} = \frac{(P_B - P_S)D_\lambda^*}{\sqrt{\Delta f A_D}}\,. \tag{7}$$

The minimum detectable power change is therefore

$$(P_B - P_S) = \frac{t\sqrt{(2\,\Delta f A_D)}}{D_\lambda^* \sqrt{n}}\,. \tag{8}$$

The r.m.s. power change, $(P_B - P_S)$, in W, due to the sample absorber only, is given[1] by

$$(P_B - P_S) = k_m W s I^0 T_B[1 - \exp(-2{\cdot}3\varepsilon_\lambda\, bC)], \tag{9}$$

and if C is C_{mt}, then

$$(P_B - P_S) = 2{\cdot}3 k_m W s I^0 T_B \varepsilon_\lambda b C_{mt}, \tag{10}$$

where W is the monochromator slitwidth, in cm (assuming entrance and exit slits have equal widths and heights), s is the spectral bandwidth, in mμ, of the radiation passing out of the exit slit ($s \sim R_d W$, where R_d is the reciprocal linear dispersion of the monochromator, in mμ/cm), I^0 is the source intensity in Wcm^{-2} ster^{-1} mμ^{-1}, T_B is the transmittance of the solvent-blank solution, ε_λ is the molar absorptivity of the absorber, b is the cell width of the absorbing medium, in cm, and k_m is the monochromator factor which is given by

$$k_m = H t_F \Omega, \tag{11}$$

where H is the height of the monochromator slit, t_F is the transmittance of all optical components, and Ω is the solid angle of radiation, in steradians, collected from the source by the monochromator.

Solving the above expressions, for C_{mt} results in

$$C_{mt} = \frac{t\sqrt{2}}{2{\cdot}3\sqrt{n}} \left(\frac{\sqrt{(\Delta f A_D)}}{\varepsilon_\lambda b k_m W s T_B I^0 D_\lambda^*}\right). \tag{12}$$

DISCUSSION

Plots of D_λ^* *vs.* wavelength and other characteristics for a number of infrared detectors at several temperatures are given by Kruse *et al.*[3] If accurate values are known for I^0 for the infrared source, for k_m, W and s for the monochromator, for b

and T_B for the sample cell width and blank transmittance, for A_D and $D_\lambda{}^*$ for the infrared detector, and for Δf for the amplifier-readout system, then it is possible to obtain good estimates of the theoretical minimum detectable sample concentration, in mole. l^{-1}, of any species of which the molar absorptivity at the wavelength of measurement is known. In Fig. 1, a spectral comparison is given of the theoretical minimum detectable sample concentration [calculated from equation (12)], and the practical minimum detectable sample concentration, C_{mp} [calculated from equation (1)] for a hypothetical infrared absorber (assuming ε_λ is 1·0 l. mole^{-1}cm^{-1} at all wavelengths) measured by means of a typical infrared spectrometer with typical photon-type detectors (an InSb photoconductivity detector at 295°, 195° and 77°K) and a typical thermal-type detector (a radiation thermocouple at 295°K). The shapes of the C_{mt} curves in Fig. 1 are determined predominantly by the spectral detectivity, $D_\lambda{}^*$, and to a lesser extent by the variation in source intensity, I^0 for the photon-type detector, and are determined completely by the source intensity for the thermal-type

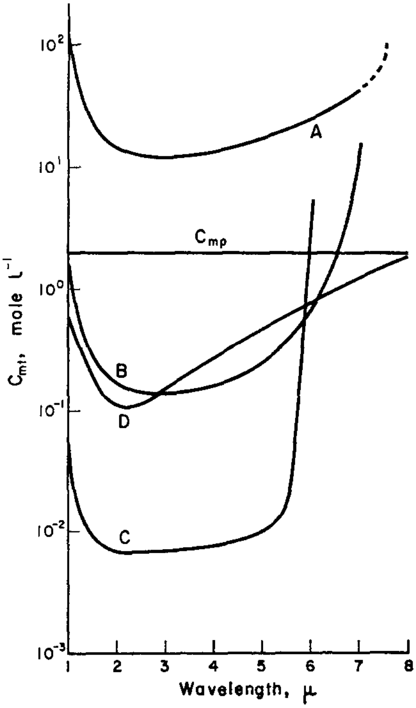

FIG. 1.—Plots of C_{mp} [calculated from equation (1), assuming $A_{min} = 0{\cdot}02$ and $b = 0{\cdot}01$ cm] and C_{mt} [calculated from equation (12), assuming $n = 6$ and $t\sqrt{2}/\sqrt{n}$ for 99·5% confidence level is 2·0), for an infrared absorber ($\varepsilon_\lambda = 1{\cdot}0$ at all wavelengths) and a typical infrared spectrometer.

The parameters used to obtain C_{mt} were: $\Delta f = 1$ Hz; $b = 0{\cdot}01$ cm; $k_m = 2{\cdot}5 \times 10^{-3}$ cm ster; $W = 0{\cdot}01$ cm; $s = 0{\cdot}01\ \mu$; $T_B = 0{\cdot}5$; $A_D = 0{\cdot}04$ cm^2; I^0 for a Nernst glower at a temperature of 1400°K and an emissivity of 0·8 at all wavelengths between 1 and 10 μ was calculated from Planck's equation to be 0·161, 0·875, 0·659, 0·386, 0·224, 0·135, 0·0851, 0·0558, 0·0340, and 0·0266 w cm^{-2} ster^{-1} μ^{-1} at 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 μ respectively. The $D_\lambda{}^*$ values for an InSb photoconductivity detector at (*A*) 295°K, (*B*) 195°K, and (*C*) 77°K and the D^* values for a thermocouple at (*D*) 295°K were taken from ref. 3.

detector (D^* is constant at all wavelengths). It has been assumed in performing the calculations for Fig. 1 that the slitwidth, the spectral bandwidth and the transmittance of the monochromator system remain constant (at the values specified in the caption) for all wavelengths. It is well-known that certain infrared detectors are best suited to give low limits of detection and sharp spectra only over a limited wavelength range. By use of plots similar to those given in Fig. 1 the optimum detector for a given study can be chosen. It should also be noted that the minimum detectable sample concentration can be easily estimated from the general plots such as those in Fig. 1 by dividing the value of the concentration at the proper wavelength by the molar absorptivity for the species concerned. It is further apparent from a comparison of the C_{mt} and C_{mp} plots in Fig. 1 that the value of C_{mp} can only be considered a rough estimate of the minimum detectable sample concentration. If more accurate estimates of the minimum detectable sample concentration are required, or if an infrared instrument has characteristics differing from those used in Fig. 1, then equation (12) must be used, assuming of course, that reasonably correct values of the requisite parameters are known.

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Zusammenfassung—Es wird ein Ausdruck angegeben, der die Berechnung der geringsten nachweisbaren Probenkonzentration für ein absorbierendes Molekül gestattet, bei Messung an einem beliebigen Infrarot-Spektrophotometer mit thermischem oder optischem Detektor. Für ein hypothetisches absorbierendes Medium mit einem molaren Extinktionskoeffizienten von Eins und für mehrere verschiedene optische und thermische Detektoren werden typische Diagramme der kleinsten nachweisbaren Probenkonzentration gegen die Wellenlänge angegeben. Solche Diagramme sind zusammen mit dem allgemeinen Ausdruck von Nutzen bei der Auswahl des besten Detektors für eine gegebene Infrarotmessung und zur Ermittlung der kleinsten nachweisbaren Probenkonzentration, die an einem gegebenen spektrometrischen System gemessen werden kann.

Résumé—On donne une expression qui permet de déterminer la concentration minimale décelable d'un échantillon d'un absorbeur moléculaire au moyen de n'importe quel spectrophotomètre infra-rouge utilisant des détecteurs à photons ou thermiques. On donne des courbes typiques de la concentration d'échantillon minimale décelable en fonction de la longueur d'onde pour un absorbeur hypothétique avec une absorption moléculaire égale à l'unité et pour plusieurs détecteurs à photons et thermiques différents. De tels graphiques, utilisés en même temps que l'expression générale, sont utiles pour sélectionner le détecteur optimal pour une mesure infra-rouge donnée et pour l'estimation de la concentration minimale d'échantillon décelable mesurée par un système spectrométrique spécifique.

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APPENDIX

Relationship Between D_λ^* and γ

Photoanodic Sensitivity for a Photoemissive Phototube

In previous papers by Winefordner *et al.*,[1,7-11] a parameter γ, the spectral response (in A at the photoanode per watt of radiant power at the photocathode, has been used to derive the signal-to-noise ratio. It is related to R_λ by

$$R_\lambda = \gamma R_L, \tag{13}$$

where R_L is the load resistor across which the voltage output is measured. However, owing to the complexity of the signal and noise terms in the infrared region, the parameter D_λ^* is used which inherently contains the signal-to-noise ratio. It is of interest to relate γ to D_λ^*. By substitution of equation (13) into equation (6), γ can be defined as

$$\gamma = \frac{V_N D_\lambda^*}{R_L(A_D\Delta f)^{1/2}}.$$

The noise term V_N is not the total noise of the system, but is rather only the shot noise due to the phototube. Therefore if equation (12) is used for any photoemissive-type detector, it must be made certain that the system is shot-noise limited.

Talanta, 1968, Vol. 15, pp. 213 to 219. Pergamon Press. Printed in Northern Ireland

CHROMATOGRAPHIC SEPARATION OF DIASTEREOISOMERIC ESTERS—II

MANDELATES AND LACTATES OF 2-METHYLBUTANOL-1, 3-METHYLBUTANOL-2, PENTANOL-2 AND HEXANOL-2

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Summary—The racemic alcohols, 2-methylbutanol-1, 3-methylbutanol-2, pentanol-2 and hexanol-2 have been esterified with optically active mandelic or lactic acid, and the resultant mixtures of diastereoisomeric esters separated chromatographically with an optically inactive sulphonated polystyrene resin as the stationary phase and water or dilute aqueous sodium sulphate as the mobile phase. Lactate esters were more easily separated than mandelate esters. The chromatographic separation of 26 mmole of (±)-3-methyl-2-butyl(+)-lactate and subsequent hydrolysis of the fractions containing only the ester of the (+)-alcohol yielded 1·2 mmole of pure 3-methyl-2-butanol.

EARLIER work[1] in this laboratory was concerned with the esterification of (±)-s-butanol with (−)-mandelic acid and the chromatographic separation of the resulting diastereoisomers, Dowex 50W-X2 serving as the stationary phase and water as the eluent. Each diastereoisomer (~7 mmole) was obtained almost 100% pure, as a dilute aqueous solution (0·003–0·006*M*). It was also found that larger yields of the resolved butanol-2 could be obtained by the use of optically active lactic acid instead of mandelic acid because of the greater solubility of the lactate ester in water. This paper describes similar work with other alcohols and again demonstrates the superiority of the lactate esters.

EXPERIMENTAL

Synthesis of the esters

Research-grade chemicals were used throughout this study. Optical purity of the acids was checked by polarimetry before use, and the alcohols were checked for purity by gas chromatography on polar and non-polar columns.

The (±)-2-pentyl (−)-mandelate was prepared by Professor John M. Cross of the Rutgers College of Pharmacy. To prepare the other mandelate esters, 740 mmole of alcohol, 1100 mmole of mandelic acid, 75 ml of benzene and 5 g of concentrated sulphuric acid were heated in a round-bottom flask under reflux with magnetic stirring. Water from the esterification was trapped in a Dean-Stark tube. When the amount of water indicated complete esterification of the acid, the mixture was cooled and shaken with aqueous sodium carbonate to neutralize the sulphuric acid and possibly some unreacted mandelic acid. The mixture was dried with sodium sulphate, and the benzene was removed by distillation. The ester was then purified by fractional distillation under low pressure.

The lactic acid was purchased as a 40% solution in water. Some of this water was removed by distillation and trapping in the Dean-Stark tube before the alcohol was added to the reaction mixture. Except for this, the lactate esters were prepared by the same method as the mandelates.

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The properties of the esters are given in Table I. The solubilities of the mandelates were determined by the method previously described.[1] The same method was used for the lactates except that the saturated solution was analysed by the dichromate method[1] instead of the spectrophotometric procedure.

Chromatography

The sodium form of Dowex 50W-X2, 200–400 mesh, was used in all the chromatographic experiments. The resin had been previously treated by the standard procedure to remove foreign ions and (as far as practicable) soluble organic compounds. Liquids were pumped through the columns at constant flow-rates. All chromatographic separations were performed at room temperature except one, which is discussed later. In some preliminary elutions, the eluates were monitored automatically with a recording spectrophotometer at 2570 Å (mandelates) or 2300 Å (lactates). Unfortunately, there was a continuous bleeding from the resin, of organic materials with very large absorptivities in the ultraviolet. This led to large and variable blank corrections. Therefore, for accurate study of the chromatographic separations, fractions of equal volume (usually 7·54 ml) were collected; aliquots of these were analysed by the dichromate method.[1] The concentration of organic matter from the resin was small and gave only small blank corrections. In almost all cases, polarimeter readings, accurate to 0·005°, were also taken. From these two sets of results, the concentration of each diastereoisomer in the fraction was calculated.

Values of the distribution ratio, *C*, and the number of plates in the column, *p*, were calculated from elution graphs by use of the equations of Beukenkamp *et al.*[2] The same parameters were calculated from frontal graphs by the equations of Spitz *et al.*[3] The interstitial volume was taken as 30% of the column volume.[4]

Experimental conditions such as the length of column and flow-rate are given in the next section. Flow-rates are expressed in cm/min, *i.e.*, ml of effluent per min divided by the cross-sectional area of the column.

RESULTS AND DISCUSSION

(±)-2-*Methyl*-1-*butyl* (±)-*mandelate*

The esterification of racemic 2-methylbutanol-1 with racemic mandelic acid yields a mixture of four diastereoisomers. It was hoped that this mixture could be separated into a mixture of the D–D and L–L esters and a mixture of the D–L and L–D esters. However elution with water at 0·19 cm/min through a 217-cm column gave a single peak with a distribution ratio of 25·2. Because of the small solubility of this compound

Table I.—Properties of the esters

Ester	Melting point, °*C*	Boiling point, °*C*	Solubility, *mole/l*	Specific rotation
(±)-2-methyl-1-butyl (±)-mandelate	18·5–20	127–130 at 4 mm	0·00346 in H_2O	$[\alpha]_D = 0{\cdot}0$
(±)-3-methyl-2-butyl (−)-mandelate	62–64	154–158 at 15 mm	0·00396 in H_2O	$[\alpha]_D^{22} = -90{\cdot}2$ (2·48 g/100 ml, benzene)
(±)-2-pentyl (−)-mandelate	27–28		0·00400 in H_2O	$[\alpha]_D^{25} = -91{\cdot}5$ (0·088 g/100 ml, H_2O)
(±)-3-methyl-2-butyl (+)-lactate		33–35 at 2 mm	0·10 in H_2O 0·055 in 0·50*M* Na_2SO_4	$[\alpha]_D^{23} = -6{\cdot}01$ (0·532 g/100 ml, H_2O)
(±)-2-pentyl (+)-lactate		40–42 at 3 mm	0·11 in H_2O 0·056 in 0·50*M* Na_2SO_4	$[\alpha]_D^{24} = -3{\cdot}55$ (1·78 g/100 ml, H_2O)
(±)-2-hexyl (+)-lactate		40–43 at 1 mm	0·25 in H_2O 0·0090 in 0·50*M* Na_2SO_4	$[\alpha]_D^{20} = -4{\cdot}97$ (0·200 g/100 ml, H_2O)

in water and its large C value, the use of aqueous salt solution as eluent to improve the separation was not practicable. Failure to separate this mixture of diastereoisomers is convincing proof that the esters of the racemic alcohol with active mandelic acid can not be separated by this method. Therefore work with this alcohol was abandoned.

It is interesting to note that Rose *et al.*[5] were unable to separate by gas–liquid chromatography the diastereoisomeric esters of 2-methylpentanol-1 with optically active acids. It seems that the hydroxyl group of an alcohol must be attached to the asymmetric carbon atom if its diastereoisomeric esters are to be separable by chromatography.

(±)-2-*Pentyl* (—)-*mandelate*

Elution of this ester with water through a 312-cm column at 0·27 cm/min failed to give any evidence of separation. There was a single tailing peak corresponding to $C = 18{\cdot}5$.

(±)-3-*Methyl-2-butyl* (—)-*mandelate*

A preliminary elution of this ester with water through a 115-cm column gave a graph with two badly overlapping peaks. A longer column (218 cm) was then used.

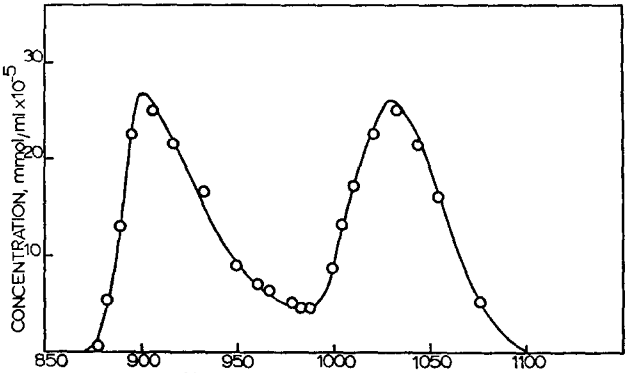

FIG. 1.—Elution of (±)-3-methyl-2-butyl (—)-mandalate.
Sample: 10·0 ml of 0·00430*M* (±)-3-methyl-2-butyl (—)-mandelate.
Column: 218 cm × 0·785 cm^2 of Dowex 50W-X2, 200–400 mesh, sodium form.
Eluent: water at 0·18 cm/min.

Fractions of 5·54 ml of eluate were collected and analysed by the dichromate method. The graph is shown in Fig. 1. The fractions of the second peak had more negative rotations than those of the first peak, indicating that the ester of the (+)-alcohol is eluted first. The retention volumes (U^*) of the two esters were used to calculate the distribution ratios (C values), which were 16·3 and 18·8. It was also calculated from the graph that there were 10·4 and 5·6 plates/cm for the first and second isomers respectively. From these data, it was calculated that a column of 313 cm would give a separation 99·9 % complete. This is in good agreement with the result (320 cm) calculated from the graph of the elution with the 115-cm column.

When the flow-rate was increased from 0·18 to 0·42 cm/min, the elution curve was similar to that of Fig. 1 but there was a minor increase in the C values (16·7 and 19·2) and a marked change in the number (P) of plates/cm (5·9 and 6·3).

(±)-2-*Pentyl* (+)-*lactate*

Five ml of a 0·112*M* solution of this ester were put on a column, 312 cm × 0·785 cm^2, and eluted with water at 0·23 cm/min. The elution graph (Fig. 2) shows that a partial separation was achieved. The *C* values calculated from the two peaks were 4·63 and 4·85. The number of plates per cm was 18 for the first isomer and 16 for the second, calculated from the rising slope of the first curve and from the falling slope of the second. It would require a column 14 m long to give a quantitative separation of the two diastereoisomers. Fractions corresponding to the first elution curve had negative rotations while those of the second had positive rotations. This indicates that the (—)-pentyl (+)-lactate precedes its diastereoisomer.

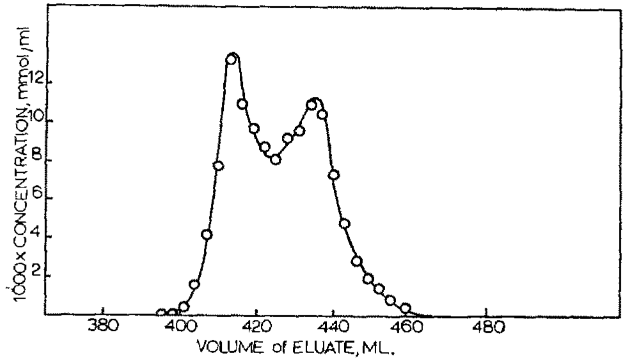

Fig. 2.—Elution of (±)-2-pentyl (+)-lactate.
Sample: 5·00 ml of 0·112*M* (±)-2-pentyl (+)-lactate.
Column: 312 cm × 0·785 cm^2 of Dowex 50W-X2, 200–400 mesh, sodium form.
Eluent: water at 0·23 cm/min.

(±)-2-*Hexyl* (+)-*lactate*

Ten ml of a 0·0248*M* solution of this ester were eluted under the same conditions as those of Fig. 2. The graph showed a partial separation. Again the ester of the (—)-alcohol was eluted first. *C* values were 6·69 and 7·09. Calculation indicated that a column 29 m in height would be required for a quantitative separation.

(±)-3-*Methyl-2-butyl* (+)-*lactate*

A sample of 0·50 mmole of this ester was eluted with water at 0·26 cm/min through a column, 324 cm × 0·785 cm^2. The elution graph indicated a significant partial resolution with *C* values of 3·91 and 4·35, and 5·1 and 7·3 plates/cm. It was calculated from these data that an 800-cm column would give a quantitative separation.

Very many chromatographic separations of organic non-electrolytes can be greatly improved by using an aqueous salt solution[6,7] instead of pure water as the eluent. Accordingly, the next experiment was the elution of 0·55 mmole of this ester with 0·50*M* sodium sulphate at 0·25 cm/min through a column, 319 cm × 0·785 cm^2. The elution graph (Fig. 3) shows a nearly quantitative separation with *C* values of 10·1 and 11·3 and *P* values of 5·1 and 7·3 plates/cm, indicating that quantitative separation would be achieved with a 420-cm column.

Effect of temperature. To test the effect of temperature, two elutions were performed under nearly identical conditions except for temperature; one was performed at room temperature (about 25°), the other in a room thermostatically controlled at 5°. The results are summarized in Table II. Clearly, the use of low temperature has a deleterious effect on this separation.

TABLE II.—EFFECT OF TEMPERATURE ON THE ELUTION OF (±)-3-METHYL-2-BUTYL (+)-LACTATE WITH WATER

t, °C	C_1	C_2	P_1	P_2	Column height for complete separation, *cm*
25	3·91	4·35	5·1	7·3	800
5	6·01	6·43	5·2	2·9	2900

Repetitive frontal chromatography. With a column of a given size, larger quantities of sample can be separated by this method[3] than by either elution or simple frontal chromatography. Three 280-ml portions of 0·307*M* (±)-3-methyl-2-butyl (+)-lactate were pumped through a column, 317 cm × 0.785 cm^2, of Dowex 50W-X2. The interstitial volume of this column was 70·2 ml. The first and second portions of sample were each followed by 280 ml of water. After the third portion, water was pumped through the column until all the ester was removed. A flow-rate of 0·25 cm/min was maintained. Eluate fractions of 7·54 ml were collected and examined polarimetrically, and the esters were determined in 1·00-ml aliquots of the fractions by the dichromate procedure.

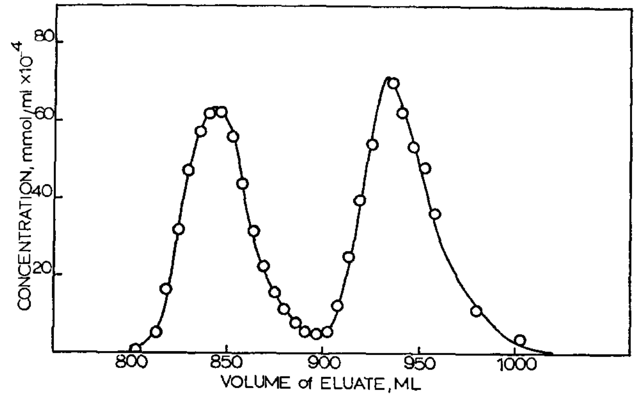

FIG. 3.—Elution of (±)-3-methyl-2-butyl (+)-lactate.
Sample: 10·0 ml of 0·0546*M* (±)-3-methyl-2-butyl (+)-lactate.
Column: 319 cm × 0·785 cm^2 of Dowex 50W-X2, 200–400 mesh, sodium form.
Eluent: 0·50*M* sodium sulphate at 0·25 cm/min.

Figure 4 is the graph of the emergence of the first portion of 280 ml of 0·0307*M* ester solution. The graphs of the emergence of the second and third portions have essentially the same shape as the first but are displaced along the abscissa by 560 and 1120 ml respectively. The interpretation of this type of chromatogram has been discussed elsewhere.[3] From the appropriate rising and falling parts of the three graphs, it was calculated that the mean distribution ratio of the first diastereoisomeric ester is 10·2 (standard deviation 0·25). Similar calculations for the second diastereoisomer yielded a mean distribution ratio of 11·6 (s.d. 0·15). These values are in satisfactory agreement with those found by elution chromatography (10·1 and 11·3). On the other hand, very discordant values of the number of plates/cm were obtained from the data of the repetitive frontal graph. Spitz[3] also found good agreement among the *C* values and very poor agreement among the *P* values in the separation of the diastereoisomers of 2-butyl mandelate by repetitive frontal chromatography.

Recovery of (+)-*3-methylbutanol-2.* The fraction on the third plateau of Fig. 4 had more positive rotations than those on the first plateau. This indicates that the ester of (+)-3-methyl-butanol-2 emerged from the column after the ester of the (—)-alcohol. The area under the curve of Fig. 4 from 1120 to 1265 ml of eluate corresponds to 0·9 mmole of (+)-3-methyl-2-butyl lactate. Similar areas under the graphs for the second and third sample bands correspond to 0·7 and 1·1 mmole, giving a total of 2·7 mmole of this diastereoisomer. However, 0·5 mmole had been destroyed by the application of the dichromate method to aliquots of the eluate fractions. The solutions containing the remaining 2·2 mmole of (+)-3-methyl-2-butyl lactate were combined, and the ester was extracted with ether. The ether was removed by fractional distillation, and the residue was mixed with 12 ml of 1·0*M* potassium hydroxide and refluxed on a hot water-bath for 3 hr to hydrolyse the ester. The mixture was cooled. Two grammes of sodium chloride were added and the alcohol was extracted with two 5-ml portions of ether. Fractional distillation through a 13-cm column was used to remove the ether. The optically active alcohol was then dissolved in absolute ethanol and diluted with the same solvent to 25·0 ml.

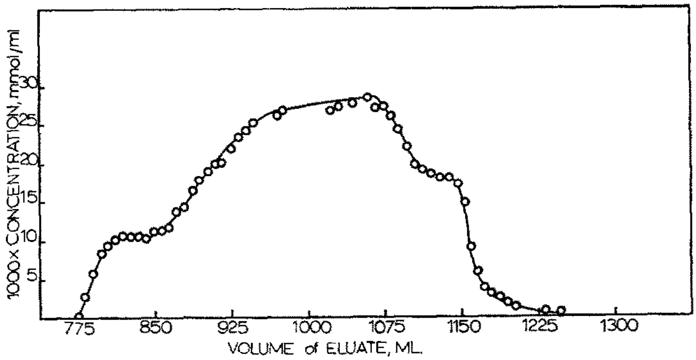

Fig. 4.—First sample band in repetitive frontal chromatography.
Sample: 280 ml of 0·0307*M* (±)-3-methyl-2-butyl (+)-lactate.
Column: 317 cm × 0·785 cm² of Dowex 50W-X2, 200–400 mesh, sodium form.
Eluent: 0·50*M* sodium sulphate at 0·25 cm/min.

The rotation of this solution with sodium D light in a 2-dm tube was +0·045°. This corresponds to 1·2 mmole of (+)-3-methylbutanol-2.

CONCLUSIONS

Optically active secondary alcohols can be obtained at essentially 100% optical purity by repetitive frontal chromatography of their esters with optically active acids, optically inactive ion-exchange resins and aqueous eluents being used. Lactate esters are preferable to mandelate esters since they are more soluble in water and hence have smaller distribution ratios. A more detailed description of this work can be found elsewhere.[8]

Acknowledgements—The authors express their gratitude to the U.S. Public Health Service for partial support of this work (Grant GM-09687) and to Prof. John M. Cross for the sample of (±)-2-pentyl (−)-mandelate.

Zusammenfassung—Die racemischen Alkohole 2-Methylbutanol-1, 3-Methylbutanol-2, Pentanol-2 und Hexanol-2 wurden mit optisch aktiver Mandel- oder Milchsäure verestert und die entstandenen Gemische diastereomerer Ester chromatographisch mit einem optisch inaktiven sulfonierten Polystyrolharz als stationärer und Wasser oder verdünntem wäßrigem Natriumsulfat als mobiler Phase getrennt. Die Lactatester ließen sich leichter trennen als die Mandelate. Die chromatographische Trennung von 26 mMol (±)-3-Methyl-2-butyl-(+)-lactat und folgende Hydrolyse der Fraktionen, die nur den Ester des (+)-Alkohols enthielten, ergab 1,2 mMol an reinem 3-Methylbutanol-2.

Résumé—On a estérifié les alcools racémiques, 2-méthylbutanol-1,3-méthylbutanol-2, pentanol-2 et hexanol-2 par les acides mandélique ou lactique optiquement actifs, et les mélanges résultants d'esters diastéréoisomères ont été séparés chromatographiquement au moyen d'une résine de polystyrène sulfoné optiquement inactive comme phase stationnaire et d'eau ou d'une solution aqueuse diluée de sulfate de sodium comme phase mobile. Les esters lactiques ont été séparés plus aisément que les esters mandéliques. La séparation chromatographique de 26 mmole de (±)-3-méthyl 2-butyl-(+)-lactate et l'hydrolyse ultérieure des fractions ne contenant que l'ester de l'alcool-(+) a fourni 1,2 mmole de 3-méthyl 2-butanol pur.

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SUBSTITUTED ETHAN PHOSPHONIC ACID ESTERS AS REAGENTS FOR THE SEPARATION OF MOLYBDENUM FROM RHENIUM BY SOLVENT EXTRACTION

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Summary—New esters of the ethan phosphonic acids have been synthesized and their extraction properties studied with respect to Mo(VI), Re(VII), Fe(III), Au(III), Tl(III) and Sb(V). A possibility is shown for the analytical separation of molybdenum from rhenium ($\beta = 700$). The state of these new extraction agents in carbon tetrachloride solution, and the mechanism of the extraction processes, have been investigated by means of infrared spectra.

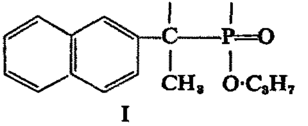
A GREAT many organo-phosphorus compounds (phosphates, phosphonates, phosphinates, and phosphine oxides), synthesized during the last two decades, have been used for analytical and industrial separation of substances.[1–4] The presence of P=O as a functional group is characteristic of all these compounds. The oxygen of that group has a free electron pair and is sterically accessible, and its bond with phosphorus is polarized, these being circumstances which determine its reactivity. Organo-phosphorus compounds of this type solvate co-ordinately a number of complex metal ions, through a donor–acceptor or other kind of bonding, enabling extraction to be made.[5–12]

Organo-phosphorus compounds prove to be rather good but not very selective extracting agents. Their selectivity could be improved (usually at the expense of their extracting ability) if electronegative substituents were incorporated into the molecule, weakening the donor properties of oxygen. Selectivity is also improved by the presence of steric effects.[13–17]

The purpose of the present work was to investigate the extraction properties of some new organo-phosphorus compounds with respect to the ions of rhenium(VII), molybdenum(VI), *etc.* The new compounds are esters of the hydroxy-naphthylethane and the hydroxy-phenylethane phosphonic acids. Here the polarity of the $^{\delta+}P{=}O^{\delta-}$ bond could be affected by the presence of the electronegative groups, OH, C_6H_5, $C_{10}H_7$, while the accessibility of the oxygen atom is partially screened by the ester groups. Hence, improved selective properties were to be expected.

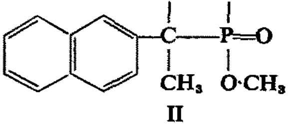
EXPERIMENTAL

The composition and structure of the five newly synthesized compounds are shown by formulas I–V.



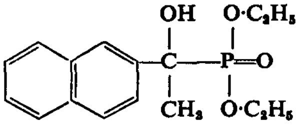
I

di-isopropyl ester of
1-hydroxy-1-β-naphthylethane
phosphonic acid (P-HNEPh)



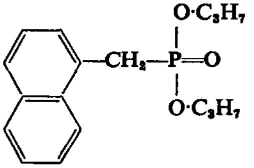
II

dimethyl ester of
1-hydroxy-1-β-naphthylethane
phosphonic acid (M-HNEPh)



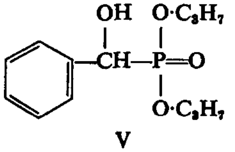
III

diethyl ester of
1-hydroxy-1-β-naphthylethane
phosphonic acid (E-HNEPh)



IV

di-isopropyl ester of
α-naphthylmethane phosphonic
acid (P-NMPh)



V

di-isopropyl ester of
hydroxyphenylmethane
phosphonic acid (P-HPhMPh)

Compound I was synthesized according to a reaction described by Abramov,[18] from di-isopropyl phosphate and methyl β-naphthyl ketone. A saturated solution of sodium methoxide in methanol is added dropwise to an equimolar mixture of these two substances. The white crystals obtained are then recrystallized from benzene. They have a specific odour and a melting point of 120–122°. Compounds II, III, and V were prepared in an analogous manner;[21] compound IV was prepared by the Michaelis–Bekker reaction.

All the compounds, except IV, are white crystalline substances with a specific odour, soluble in carbon tetrachloride, dichloroethane and trichloroethane, and partially soluble in chloroform and benzene. Therefore, the compounds can easily be obtained in a pure enough state by recrystallization.

The selective absorption of these substances in the infrared region was investigated with a Zeiss spectrophotometer UR-10. Solutions in carbon tetrachloride, dried with calcium chloride, were used for the purpose.

Extraction properties were studied with respect to the ions of molybdenum(VI), rhenium(VII), iron(III), antimony(V), thallium(III) and gold(III). The distribution coefficients, D, were determined radiometrically, by measuring the activity both in the aqueous and in the organic phase.* The radioactive isotopes used were ^{99}Mo, ^{186}Re, ^{122}Sb, ^{204}Tl, ^{198}Au. Their purity was checked by means of the gamma-spectra.

All investigations were carried out in hydrochloric acid media ranging from 1 to 10*M*. The organophosphorus compounds were used as 1 and 6% solutions in carbon tetrachloride. This solvent allowed the fastest and most thorough separation of the two phases; each phase had a volume of 12 ml.

RESULTS AND DISCUSSION

Infrared spectra of the organo-phosphorus compounds

According to the investigations of Meyrick and Thompson,[19] the selective absorption in the infrared region, due to the P=O stretching vibration in the phosphonates, appears within the range 1260–1250 cm^{-1}. The frequency of the absorption maximum of this group for the compounds used in our investigations is shown in Table I.

It is evident from these data that the energy of the P=O stretching vibration is decreased for all the compounds investigated, with the exception of IV (P-NMPh), the latter differing from the rest in that it contains no hydroxyl group. The selective

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* The distribution of Fe(III) was checked spectrophotometrically by means of 1,10-phenanthroline.

TABLE I

	Substance	ν, cm^{-1}
I	(P-HNEPh)	1235
II	(M-HNEPh)	1240
III	(E-HNEPh)	1235
IV	(P-NMPh)	1260
V	(P-HPhMPh)	1240

absorption of compound IV at 1260 cm^{-1} shows that the naphthalene ring (despite its electrophilic character), being connected with the phosphorus atom through a carbon atom, does not affect the polarity of the P=O bond. The decrease of stretching vibration frequency in the other compounds, expressed as a difference between the wave numbers, $\Delta\nu = 20$–25 cm^{-1}, could be assigned to intermolecular or intramolecular interaction, resulting from the formation of a hydrogen bond between the phosphoryl and the hydroxyl groups. It should be noted that the infrared spectrum of the crystalline substance, dispersed in Nujol (Fig. 1) is identical with the spectrum of a 6% solution of the same substance in carbon tetrachloride; the P=O stretching vibration occurs at the same wave numbers. This proves that in the solution most of the molecules are combined in polymers.

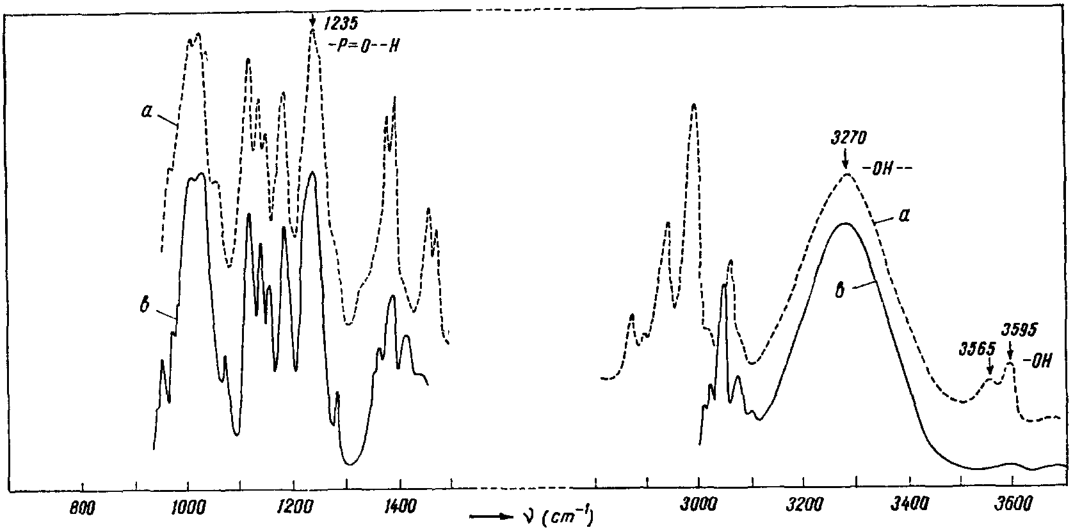


FIG. 1.—Infrared spectrum of compound I (P-HNEPh).
(*a*) 6% solution in CCl_4; (*b*) dispersed in Nujol.

The interactions described above are also confirmed by the character of the absorption of the hydroxyl group. Three absorption maxima are observed with a 1% solution of compound I in carbon tetrachloride: a wide, intensive maximum at 3270 cm^{-1} and two sharp, less intensive ones, at 3565 and 3595 cm^{-1} (Fig. 2, curve *a*). With the extraction of molybdenum or iron, the spectrum of the extract is different; a new maximum appears at 3435 cm^{-1} (Fig. 2, curve *b*). The intensity of this maximum increases with increase of molybdenum concentration, at the expense of the maximum

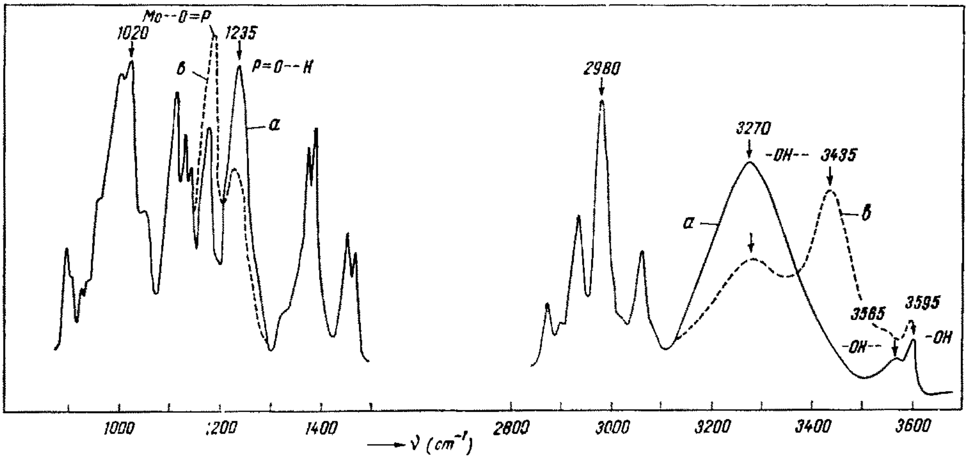
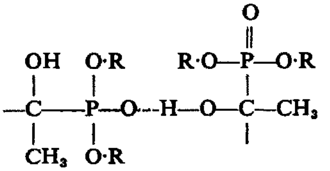


FIG. 2.—Infrared spectra of (*a*) 1% solution of compound I (P-HNEPh) in CCl_4, (*b*) an extract of Mo with the same compound.

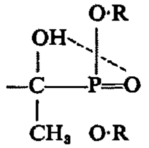
at 3270 cm^{-1}. A shift of the absorption of P=O ($\Delta\nu = 45\ cm^{-1}$) is also observed in the molybdenum extract.

The absorption at 3595 cm^{-1} evidently corresponds to a free hydroxyl group, not affected by other interactions. The intensive absorption in the region about 3270 cm^{-1}, corresponding to a rather strong hydrogen bond ($\Delta\nu = 325\ cm^{-1}$), could be assigned both to an intermolecular hydrogen bond (VI), and to intramolecular ones, (VII) and (VIII):

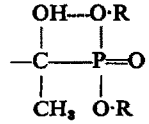


$$-\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\underset{\text{O·R}}{\overset{\text{O·R}}{\text{P}}}-\text{O}\cdots\text{H}-\text{O}-\underset{|}{\overset{\text{R·O}-\overset{\overset{\text{O}}{\|}}{\text{P}}-\text{O·R}}{\text{C}}}-\text{CH}_3$$

VI



VII



$$-\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\underset{\text{O·R}}{\overset{\text{O·R}}{\text{P}}}=\text{O}$$

VIII

The maximum at 3565 cm^{-1} shows the formation of a very weak hydrogen bond, most probably between the OH-group and the π-electrons of the naphthyl ring.

When an atomic model is made of the structure of the compound under consideration, it is evident that the phosphoryl oxygen atom is sterically accessible and it is possible for there to be an intermolecular hydrogen bond between this atom and the hydroxyl group of another molecule. In this way both dimers and polymers could be obtained. Intramolecular bonds between the hydroxyl group and the oxygen of the phosphorus, as well as between the hydroxyl group and the oxygen atom of the ester, are also possible. Under definite conditions of concentration and temperature, an equilibrium could be expected to be maintained between the molecules of the ester which are free from interaction and those with an intramolecular or intermolecular hydrogen bond. From the most general thermodynamical considerations, accounting for the basicity of the phosphoryl and the ester oxygen atoms, it follows that the intermolecular hydrogen bond (VI) and the intramolecular one (VII) will be preferred.

With the purpose of clarifying the origin of the absorption at 3270 cm^{-1}, we have taken the infrared spectra of solutions of compound I, with a concentration within the range $1{\cdot}8 \times 10^{-1}$–$1{\cdot}8 \times 10^{-4}M$. The maximum at 3270 cm^{-1} is decreased only at very high dilution, a maximum at about 3430 cm^{-1} appearing simultaneously. There is reason for the assumption that the hydrogen bonds in structures VI and VII will be very close in strength and that the valence variations of the hydroxyl group will be manifested in a single, wider and more intensive maximum. Upon dilution, the hydrogen bond of type VI will be broken, making possible the formation of bonds of types VII and VIII in the freed molecules. From a thermodynamical point of view, a bond of type VII should be preferred, but as is evident from the model structure, under some conditions there will be kinetic barriers to its formation, on account of which a bond of type VIII will also be formed and sterically preferred. The shift of the absorption from 3270 to 3430 cm^{-1}, in the extraction of molybdenum or iron, could be assigned to alteration of the absorption of the hydroxyl group upon co-ordinative solvation.

Extraction properties of the organo-phosphorus compounds

The extraction properties of compound I have been studied with respect to the ions of Re(VII), Mo(VI), Au(III), Fe(III), Sb(V), and Tl(III). Figure 3 shows the relationship between log D and the concentration of hydrochloric acid. It is evident that molybdenum, gold, iron, antimony, and thallium can be extracted relatively well, whereas the extraction of rhenium is rather limited. This condition enabled relatively good separation of molybdenum from rhenium to be made by extraction and restricted our further investigations to these two elements only.

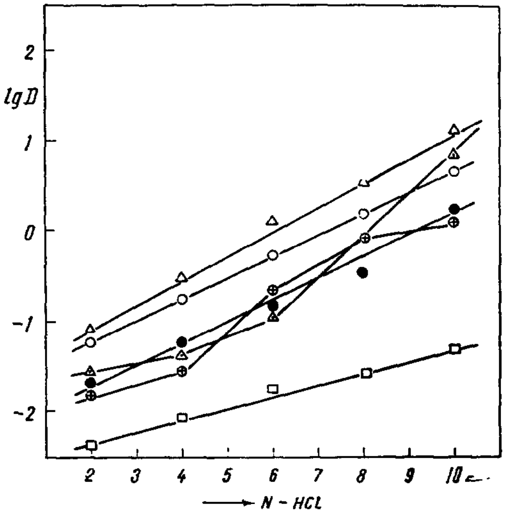


FIG. 3.—Relationship between log D and the concentration of hydrochloric acid. Extraction with a 6% solution of compound I: △—Mo; ○—Au; ●—Fe; ◬—Sb; ⊕—Tl; □—Re.

The relationship between log D and the concentration of hydrochloric acid in the extraction of molybdenum and rhenium was studied with compounds I, IV, and V. It is evident from Fig. 4 that with solutions of not too high acidity ($6M$ hydrochloric acid), convenient for work, the best separation of the two elements is achieved with compound V (separation factor, $\beta = 700$).

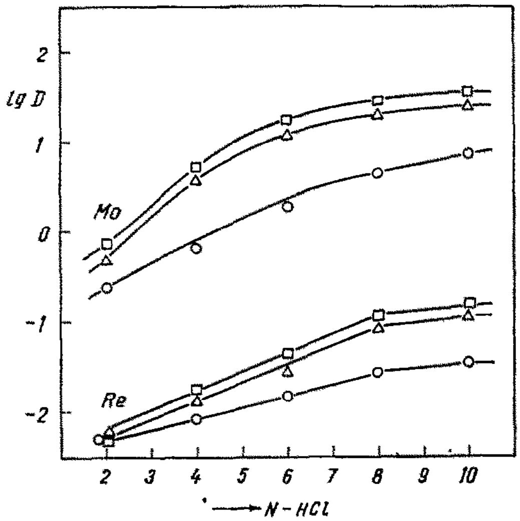


FIG. 4.—Relationship between log D and the concentration of hydrochloric acid. Extraction with a 6% solution of the following compounds: □—V (HPhMPh); △—I (P-HNEPh); ○—IV (P-NMPh).

For the analytical separation of molybdenum from rhenium by this method, it was important to study the effect of the presence of sulphate ions on the distribution coefficient. Experiments proved that the presence of 0·5 g of sodium sulphate in the volume used does not interfere.

Mechanism of extraction

The great difference between the distribution coefficients of molybdenum and rhenium is probably due to the different extraction mechanism of the two metals, which could be attributed to the nature of their complexes.

Over a very wide concentration range of hydrochloric acid, rhenium is present in the form of the perrhenate ion, ReO_4^-. Molybdenum(VI), however, forms, depending on the acidity, various types of complex with the ratio Mo:Cl = 1:2 and 1:3. According to Neumann and Cook,[20] the probable compositions of these complexes are MoO_2Cl_2, $MoO(OH)_2Cl_2$, and $MoO(OH)Cl_3$. Taking into consideration the large positive charge of Mo^{6+}, these neutral complexes should have a covalent character.

When the strong shift of the maximum of valence variations of P=O (Fig. 2) is taken into account, it seems very probable that the extraction of molybdenum is due to a co-ordinative solvation of the molybdenum chloride complexes. With rhenium, all co-ordination sites are occupied by oxygen atoms, making such a solvation impossible. The extraction of rhenium probably takes place according to a hydration–solvation mechanism, and owing to the relatively low concentration of the active extracting agent (6%) usually used, the distribution coefficient is insignificant.

Analytical application

Ten ml of the solution under investigation, made 6*M* with respect to hydrochloric acid, is extracted twice, each time with 10 ml of a 6% solution of P-HPhMPh(V) in carbon tetrachloride. The two phases are separated and the aqueous one is filtered into a 100-ml separating funnel through filter paper wetted with water. The solution is diluted with water to a convenient standard volume and rhenium is determined by the thiocyanate method.

Zusammenfassung—Neue Ester der Äthan Phosphonsäuren wurden dargestellt und ihre Extraktionseigenschaften mit Mo(VI), Re(VII), Fe(III), Au(III), Tl(III) und Sb(V) untersucht. Eine Möglichkeit zur analytischen Trennung von Molybdän und Rhenium ($\beta = 700$) wird gezeigt. Der Zustand dieser neuen Extraktionsmittel in Tetrachlorkohlenstofflösung und der Mechanismus der Extraktionsprozesse wurde mit Hilfe von Infrarotspektren untersucht.

Résumé—On a synthétisé de nouveaux esters d'acides ethan phosphoniques et étudié leurs propriétés d'extraction en ce qui concerne Mo(VI), Re(VII), Fer(III), Au(III), Tl(III) et Sb(V). On révèle une possibilité de séparation analytique du molybdène du rhénium ($\beta = 700$). On a étudié, au moyen de spectres infra-rouges, l'état de ces nouveaux agents d'extraction en solution dans le tétrachlorure de carbone et le mécanisme des processus d'extraction.

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HOMOGENEOUS NUCLEATION OF CALCIUM HYDROXIDE†

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(*Received* 8 *August* 1967. *Accepted* 19 *September* 1967)

Summary—The rate of nucleation of calcium hydroxide in carefully purified supersaturated solution was observed to be about 10^3 particles. $cm^{-3}.sec^{-1}$, in solutions with activity products $a_{Ca}a_{OH}^2$ around 4×10^{-5}. These data correspond to a homogeneous nucleus containing about 55 $Ca(OH)_2$ units, and a nucleus–solution interfacial tension of 65 erg/cm^2.

The free energy for the creation of a new phase in the presence of a supersaturated mother phase is given by

$$\Delta G = -nkT \ln (c/s) + \sigma A,$$

where n = number of molecules transferred to the new phase
k = Boltzmann constant
c = concentration of the supersaturated mother phase
s = concentration of the saturated mother phase
σ = surface free energy/cm^2 of surface of the new phase
A = surface area of the new phase.

The first term on the right thus corresponds to the free energy of transfer of n molecules from the supersaturated solution to the new phase, which would be in equilibrium with a saturated solution, and the second term corresponds to the free energy required to form the surface, of area A, of the new phase. Both terms depend on n, and the degree of dependence is such that the second term is predominant at small n, and the first at large n, so that ΔG goes through a maximum. The particle of new phase for which ΔG is a maximum is defined as the nucleus, and is the smallest particle for which increase in n is a spontaneous process. The free energy of forming the nucleus, ΔG^*, can be shown to be related to the area of the nucleus, A^*, and to the number of molecules in the nucleus, n^*, by

$$\Delta G^* = \sigma A^*/3, \quad \text{and}$$
$$\Delta G^* = n^*kT \ln (c/s)/2.$$

Christiansen's theory of nucleation of precipitates from solution[1] permits calculation of ΔG^*, and hence of n^* and σ, from the rate of nucleation at a particular value of c. In addition, n^* can be determined independent of Christiansen's theory by examining the variation in nucleation rate with concentration, since a very simple steady-state approach to nucleation kinetics leads to the equation[2]

$$dN/dt = k(IP)^{n^*},$$

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† This study was aided by a grant from the Office of Saline Water, U.S. Department of the Interior.

where N = number of nuclei formed

t = time

(IP) = ion product.

Thus a plot of $\log dN/dt$ against $\log (IP)$ has slope n^*, and from n^* it is possible to calculate ΔG^* and σ by using the equations given above.

In studies of the nucleation of strontium sulphate[2] and magnesium hydroxide,[3] sufficient data were obtained to permit calculation of ΔG^*, n^*, and σ both by the steady-state approach, and by Christiansen's theory. The good agreement between the values gives strong support to the theory.

The steady-state approach requires that (IP) be varied over a very small range, because n^* is rather large, and if n^* is too large, it is experimentally very difficult to use this method. Preliminary experiments in the present study of nucleation of calcium hydroxide indicated that n^* was too large for the steady-state approach to be experimentally useful, and so the results are based solely on Christiansen's theory.

The precipitate–solution interfacial tension, σ, is a key parameter for precipitation, in that it strongly influences both the nucleation rate and the rate of crystal growth by several mechanisms.[1] The surface of tension between the particle and the solution is difficult to visualize, since, because of the small size of the nucleus, the volume of this "surface" of tension may be comparable in magnitude to, or larger than, the volume of the solid phase. Whatever the surface tension is, it is clearly an important property, and so its relationship to the structure of the precipitate is of interest. The present study of nucleation of calcium hydroxide was therefore undertaken, to permit the comparison of two similar systems, calcium and magnesium hydroxides.

EXPERIMENTAL

Solutions were purified as described previously.[3] The supersaturated calcium hydroxide was prepared by slowly pumping about 30 ml of 0·50M sodium hydroxide into about 175 ml of 0·050M calcium nitrate, the pumping rate being 0·0021 ml/sec. The pH of the solution was recorded from an expanded scale pH meter, standardized against saturated calcium hydroxide solution at pH 12·454. Addition of sodium hydroxide was stopped at pH about 12·8, and samples of the reaction mixture were taken at timed intervals for particle counting with a Coulter counter equipped with a 30-μ orifice. Detectable particles began to appear about 10–20 min after addition of sodium hydroxide was stopped. In a typical experiment, the background count, representing unremoved particles and electrical noise, was about $2·5 \times 10^4$ cm^{-3}, and the maximum count observed was $7·7 \times 10^5$ cm^{-3}.

RESULTS AND DISCUSSION

In three experiments the rates of appearance of detectable particles, taken as the nucleation rates, were $9·40 \times 10^2$, $2·36 \times 10^3$, and $2·53 \times 10^3$ cm^{-3}. sec^{-1}, at pH values of 12·873, 12·866, and 12·912, and total calcium concentrations 0·0417, 0·0413, and 0·0412M respectively, corresponding to activity products, $a_{Ca}a_{OH}^2$, $4·02 \times 10^{-5}$, $3·90 \times 10^{-5}$, and $4·02 \times 10^{-5}$. The activity products were calculated from the known total concentration of calcium, $[Ca^{2+}] + [CaOH^+]$, and the observed a_{OH}, as follows: from[4] $K_1 = 25 = a_{CaOH}/a_{Ca}a_{OH}$, and a_{OH}, the ratio a_{CaOH}/a_{Ca} could be calculated. Activity coefficients of Ca^{2+} and $CaOH^+$ were estimated as 0·314 and 0·730, from the extended Debye–Hückel equation at an ionic strength of 0·232. From the ratio of activities and activity coefficients of $CaOH^+$ and Ca^{2+}, the concentration ratio $[CaOH^+]/[Ca^{2+}]$ was obtained. Since $([Ca^{2+}] + [CaOH^+])$ is known from the initial concentration corrected for dilution, $[Ca^{2+}]$ and a_{Ca} could be calculated.

The theoretical expression for the rate of nucleation of calcium hydroxide is[1]

$$\mathrm{d}N/\mathrm{d}t = (D/d^2v_0)(2\phi/3\pi kTn^*)^{1/2}\exp(-\Delta G^*/kT),$$

where D = diffusion coefficient = $2 \times 10^{-5}\,\mathrm{cm}^2.\,\mathrm{sec}^{-1}$

d = mean diameter of one Ca^{2+} and two OH^- ions = 4×10^{-8} cm (estimated from Debye–Hückel hydrated ion diameters)

v_0 = molecular volume of solvent = $3 \times 10^{-23}\,\mathrm{cm}^3$

$\phi = kT\ln(c/s) = kT\ln[(IP)/K_{sp}]$

$K_{sp} = 3{\cdot}71 \times 10^{-6\cdot4}$.

From this equation, and those given previously, the following values were calculated: $\Delta G^* = 64{\cdot}8kT$, $64{\cdot}4kT$, $66{\cdot}6kT$, $n^* = 54{\cdot}6$, $54{\cdot}9$, $56{\cdot}1$, where n^* = number of $Ca[OH]_2$ units in the nucleus, and $\sigma = 64{\cdot}7$, $64{\cdot}2$, $65{\cdot}5$ erg. cm^{-2}. Calculation of σ requires an assumption concerning the shape of the nucleus. The assumption made is that the nucleus is a rectangular parallelepiped with edge lengths proportional to the unit cell dimensions, the same assumption that was made in the case of $Mg(OH)_2$.

The surface energy of magnesium hydroxide was found to be 115 erg. cm^{-2}, about twice the value found for calcium hydroxide in the present study. The surface energy should be influenced by the same factors as the lattice energy, and since the lattice energy of calcium hydroxide is less than that of magnesium hydroxide, due to the difference in ionic radius, the direction of the change in surface energy is intuitively satisfying. Unfortunately, the difference in surface energies cannot be quantitatively rationalized.

Zusammenfassung—Die Keimbildungsgeschwindigkeit von Calciumhydroxid in sorgfältig gereinigten übersättigten Lösungen wurde als etwa 10^3 Teilchen/cm^3/sec^1 in Lösungen mit dem Aktivitätsprodukt $a_{Ca}a_{OH}{}^2$ von etwa 4×10^{-5} gefunden. Die Daten entsprechen einem homogenen Keim aus etwa 55 $Ca(OH)_2$-Einheiten und einer Grenzflächenspannung zwischen Keim und Lösung von 65 erg/cm^2.

Résumé—On a observé que la vitesse de production de germes de l'hydroxyde de calcium en solution sursaturée soigneusement purifiée est d'environ 10^3 particules. cm^{-3}. sec^{-1}, dans des solutions ayant des produits d'activité $a_{Ca}a_{HO}{}^2$ d'environ 4×10^{-5}. Ces données correspondent à un germe homogène contenant environ 55 unités $Ca(OH)_2$, et à une tension interfaciale germe-solution de 65 erg/cm^2.

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DETERMINATION OF ^{3}H AND ^{85}Kr IN AQUEOUS SAMPLES BY LIQUID SCINTILLATION TECHNIQUES[*]

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Summary—Analytical procedures have been developed for the simultaneous determination of tritium and krypton-85 in aqueous solutions by liquid scintillation techniques. The effects of sample size, amount of water and dye were investigated.

The low concentrations at which radioisotopes can be measured make them extremely valuable in research. Recently, Tsivoglou and co-workers[1] proposed the simultaneous use of two radio-tracers to determine the reaeration rate constant, K_2, in streams. Basically, the proposal involves the use of a gaseous tracer with a gas transfer coefficient that is constant relative to that of oxygen in the streams, and tritiated water, a non-gaseous tracer that functions as a dispersion indicator. Laboratory tests have already been conducted by Tsivoglou with gaseous ^{85}Kr to verify that the relationship between the gas transfer coefficients of the tracer and other gases is constant over a wide range of turbulence.

A major difficulty associated with the simultaneous use of tracers is the need for the quantitative determination of each tracer in aqueous samples. The analytical determination of ^{85}Kr in water samples by a variety of methods has already been reported.[2] Curtis *et al.*[3] measured both ^{85}Kr and tritium, as gases, by liquid scintillation. Since liquid scintillation techniques have been demonstrated to be quite effective in the analytical determination of ^{85}Kr and ^{3}H, the objective of the investigation reported here was to develop an analytical method for the simultaneous determination of gaseous ^{85}Kr, and of tritium as tritiated water, in aqueous solutions, in support of the reaeration studies mentioned above. Three requirements for any method developed were: (1) a maximum sensitivity in order to minimize the amounts of radioisotopes required; (2) a minimum of sample handling and preparation; (3) a reasonably short time for handling the analysis so that samples would not accumulate during field work.

EXPERIMENTAL

Tritium, ^{3}H, decays to stable ^{3}He with an effective half-live of 12·26 years. Several beta particles are emitted, the maximum energy being 0·018 MeV. ^{85}Kr decays to ^{85}Nb with a half-life of 10·4 yr. During its decay, 0·7% of the total activity is gamma-radiation with energy 0·52 MeV, and 99·3% is β-radiation with maximum energy 0·67 MeV.

Because of the difference in maximum energies of the two nuclides, the difference in physical states, and the other factors affecting the count rate of each nuclide, investigations were made into the possibility of using liquid scintillation counting for ^{3}H and ^{85}Kr simultaneously in a water matrix.

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To facilitate handling and to save time in preparation and counting of separate samples for each determination, consideration was also given to a procedure for the simultaneous counting of ^{3}H and ^{85}Kr in a single sample aliquot. A Packard Tri-Carb Liquid Scintillation Counter was used to count all samples. Butler's solution[4] was used as the liquid scintillator phosphor. The counting vials were glass of low potassium content.

Tritium counting

Because water acts as a quenching agent in liquid scintillation counting, one of the first questions to be answered involved the optimum sample size for effective counting. A set of quenched standard samples was prepared in which a constant volume of phosphor, 16·0 ml, was added to each vial. Increasing increments of water, ranging from 0·05 to 4·00 ml, were added to the phosphor, followed by 50 μl of tritiated water (^{3}H activity 107,800 dpm). The vial was capped and shaken, and the samples were counted.

TABLE I.—EFFECT OF WATER ON COUNTING EFFICIENCY FOR ^{3}H

Volume of water, *ml*	Efficiency, %
0·05	28·7
0·50	25·4
1·00	22·1
1·50	19·3
2·00	17·1
2·50	15·0
3·00	13·2
3·50	11·7
4·00	9·5

Table I shows the effect of the volume of water in the mixture on quenching and counting efficiency. From these results and the fact that other materials affecting the results would be present in some field samples, a sample volume of 2 ml of water was chosen, even though a larger volume would have provided higher count rates. Also, in preparing field samples for counting, a volume of 2 ml is more easily transferred than a smaller amount.

The next question that logically arose was "How reproducible is the counting procedure for a constant water volume?". To answer this, the count for a 2·0 ml volume of water was measured for 10 samples. The range of net activity was 18,002–18,582 cpm with an average of 18,392 cpm, corresponding to an efficiency range of 16·7–17·2%, average 17·1%.

Next, four sets of triplicate samples were prepared at different levels of activity to determine whether the efficiency of counting varied with count rate. The results in Table II show that it did not.

TABLE II.—EFFECT OF COUNT RATE ON EFFICIENCY FOR ^{3}H

Tritium activity added, *dpm*	Average observed activity, *cpm*	Average efficiency, %
5130	880	17·1
1071	183	17·1
213	36	16·9
42	7·2	17·1

As the main purpose of the procedure was to determine tritium in environmental samples, ^{3}H was added to water from different locations and the samples prepared for counting. In the two extreme cases of distilled water and sea-water the efficiencies were 16·9 and 16·1% respectively.

Effect of dye on counting efficiency

If ^{3}H and ^{85}Kr are placed in a stream for the purpose of determining dispersion and reaeration rate constants, some indicator must be used to determine the time at which samples should be collected. Two dyes, Rhodamine-WT and Pontacyl Pink, have received attention as water tracers because of their relatively low rate of adsorption on surfaces of rocks and muds and their ease of detection at low concentrations by fluorimetric techniques. Studies were made to determine the effect of the presence of each of these dyes on counting efficiency. Stock solutions of Pontacyl Pink and Rhodamine-WT were diluted to the desired concentrations, and 2 ml of the dye solutions were transferred by pipette into the sample vials containing 16 ml of liquid scintillator. Each vial was then spiked with ^{3}H as tritiated water and counted. The results are presented in Table III and show essentially no change in counting efficiency in samples containing less than 1 mg of either dye per litre, but as the dye concentration increases, the light absorption characteristics of the sample are altered.

TABLE III.—EFFECT OF DYE ON COUNTING EFFICIENCY FOR ^{3}H

Weight of dye in sample, *mg*	Pontacyl Pink		Rhodamine-WT	
	Activity, *cpm*	Efficiency, %	Activity, *cpm*	Efficiency, %
0	18,730	17·4	18,639	17·3
2×10^{-5}	18,541	17·2	18,601	17·2
2×10^{-4}	18,719	17·4	18,505	17·2
2×10^{-3}	18,377	17·1	18,218	16·9
2×10^{-2}	17,833	16·5	17,565	16·3
2×10^{-1}	14,061	13·0	13,897	12·9

Krypton-85 counting

The procedure for the preparation and counting of water samples containing dissolved ^{85}Kr involves additional consideration since ^{85}Kr, being a gas, tends to diffuse out of its water matrix over a period of time.

Standard samples of known ^{85}Kr concentration were prepared by dissolving a water-soluble capsule containing ^{85}Kr atoms in a clathrate cage; in a 1-gal glass bottle filled with water and closed with a rubber stopper. The capsule and the solid dissolved in the water, releasing the ^{85}Kr as a gas, which also dissolved. The ^{85}Kr–water mixture was allowed to equilibrate overnight, and a 10·0-ml sample was taken with a pressure pipette, diluted to 1·0 l. in a container that was then closed with a rubber stopper and left overnight. Samples (2 ml) were then removed from the container and slowly added to empty glass vials; 16·0 ml of scintillator were added slowly down the sides of the vial thus minimizing losses of ^{85}Kr that might have been caused by splashing. The vials were capped and shaken once. Samples of the parent solution were also taken and the ^{85}Kr concentration determined independently by the "ion-tube" method.[3]

The liquid scintillation counter was set to count the tritium pulses in one of its channels (*A*) along with approximately 12% of the ^{85}Kr pulses. The second channel (*B*) counted the remainder of the ^{85}Kr pulses. The results of counting 5 replicate samples are shown in Table IV and indicate that the counting of ^{85}Kr was not reproducible. The major difficulty appeared to be a variable loss of ^{85}Kr gas from the sample once it was mixed with the liquid scintillator, since the total volume of liquid (18 ml) did not fill the 24-ml vial, probably because of diffusion of the gas from the liquid into the air space. To solve this problem the vials, containing the samples were filled completely with liquid scintillator. The counting experiment was repeated in this way, three counting cycles being run over a period of 3 days. The results in Table V indicate there was no noticeable loss of ^{85}Kr from solution during the 3-day period.

TABLE IV.—^{85}Kr COUNTING WITH PARTIALLY FILLED VIALS

Channel *A*, *cpm*	Channel *B*, *cpm*	*A* + *B*, *cpm*	Efficiency*, %
2090	11,586	13,676	38·5
2208	11,680	13,888	39·1
2491	13,722	16,213	45·6
2284	12,538	14,822	41·7
2583	14,649	17,232	48·5

* Based on an ion-tube determination of 35,551 dpm/2·0 ml.

The results indicate that there is still some deviation, but this is primarily a result of the techniques used to transfer the water sample from the parent container to the vial. It is obvious from Table V

TABLE V.—COMPARISON OF ^{85}Kr COUNTING RESULTS FOR A 3-DAY PERIOD

Cycle 1, *cpm*	Cycle 2, *cpm*	Cycle 3, *cpm*	Mean, *cpm*	Mean efficiency, %
26,997	26,740	26,781	26,839	75·5
23,486	23,475	23,568	23,510	66·1
25,156	25,785	25,274	25,405	71·5
25,824	25,185	26,123	25,711	72·3
25,993	25,948	26,075	26,005	73·1

that one sample contained a little less than the usual amount of ^{85}Kr, which illustrates the importance of using replicate samples because an error introduced by faulty transfer would bias a single result. If that result is discarded, the mean efficiency for ^{85}Kr ranges from 71·5 to 75·5%. Another significant source of difference results from use of a pipette to transfer solutions of high activity.

To facilitate the simultaneous counting of tritium and krypton, the instrument was adjusted to decrease the proportion of ^{85}Kr counts in channel A in order to provide better separation of the observed ^{3}H and ^{85}Kr counts. This shift caused a slight decrease in the ^{85}Kr counting efficiency. The results of counting five replicate samples are shown in Table VI.

TABLE VI.—RESULTS OF COUNTING FIVE REPLICATE ^{85}Kr SAMPLES

A, *cpm*	B, *cpm*	$A + B$, *cpm*	A/B	Efficiency, %
2274	20,961	23,235	0·109	57·0
2181	20,145	22,326	0·108	54·6
2024	18,742	20,766	0·108	50·9
2195	19,987	22,182	0·110	54·5
2203	19,633	21,836	0·112	53·6

To determine whether the ratio A/B stayed constant when dye was present, several samples were prepared with varying amounts of dye and a constant concentration of ^{85}Kr. The results in Table VII show a definite change in the A/B ratio when high concentrations of dye are present. Light absorption by the dye decreases the light intensity observed by the analyser, giving the impression that more low energy events are being observed. There is no observable effect, however, at the dye concentrations expected in field samples, and, in fact, no significant effect of dye at concentrations below 20 mg/l. The effect is important for undiluted samples.

TABLE VII.—CHANGE IN A/B RATIO WITH RHODAMINE-WT DYE CONCENTRATION

Dye concentration, *mg/l*	A/B
0·1	0·109
1	0·112
10	0·115
20	0·120
50	0·141
100	0·178

SIMULTANEOUS COUNTING OF TRITIUM AND KRYPTON-85 IN A SINGLE SAMPLE

Based on the foregoing results, a procedure was devised for counting both nuclides in a single sample. The method of sample preparation was that used for ^{85}Kr analysis, *i.e.*, completely filled vials. A third channel on the analyser was also utilized. The instrument is equipped with an external ^{226}Ra source, which bombards the liquid sample with γ-rays. On striking the sample the γ-rays are diminished in energy and Compton electrons are emitted that interact with the liquid scintillator to produce a light pulse of characteristic wavelength. This emission is a function of the sample characteristics and is relatively independent of the amount of ^{3}H and ^{85}Kr activity present. The electronic pulses produced as a result of the Compton electron interactions are recorded on channel *C*. From the count rate of an unknown sample and a standard curve of efficiency *vs.* channel *C* count rate, an efficiency factor can be obtained that is used to determine the absolute disintegration rate for each nuclide. This extra channel makes it possible, for example, to correct for the effects of the dye.

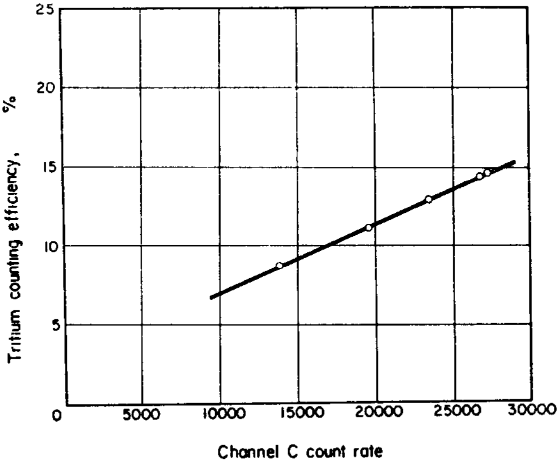

FIG. 1.—Tritium counting efficiency *vs.* channel *C* count rate.

The standard curve for ^{3}H counting was obtained by preparing a set of standards containing known amounts of tritium activity and quenched with Rhodamine-WT dye. Figure 1 shows a plot of tritium counting efficiency *vs.* channel *C* count rate. Preparation of a standard curve for ^{85}Kr was somewhat more difficult because ^{85}Kr counts are registered in both channel *A* (tritium channel) and channel *B*. As indicated above, the ratio *A*/*B* is not constant when varying amounts of Rhodamine-WT dye are present in the sample. The shift in the *A*/*B* ratio must be taken into account when samples of the undiluted mixture are analysed. It is true that the concentration of dye in the samples collected after dilution by the stream was not expected to exceed the limit at which *A*/*B* would shift but the correction factor was incorporated for cases in which the dilution was not very great. It was therefore necessary to obtain a curve for the ratio *A*/*B vs.* channel *C* count rate. This curve is shown in Fig. 2. By use of this curve and a standard curve for ^{85}Kr counting efficiency *vs.* channel *C* count rate (Fig. 3), unknown sample count rates were corrected back to an absolute disintegration rate.

When the standard curves (Figs. 1–3) are used to obtain efficiency factors for both ^{3}H and ^{85}Kr, channel *A* is first corrected for the presence of ^{85}Kr counts. Equations (1) and (2) are used to calculate the concentrations of ^{3}H and ^{85}Kr in dpm in a single sample.

$$^{3}\text{H} = \frac{A_{T+K} - X(B_K)}{E_T} \tag{1}$$

$$^{85}\text{Kr} = \frac{B_K + X(B_K)}{E_K} \tag{2}$$

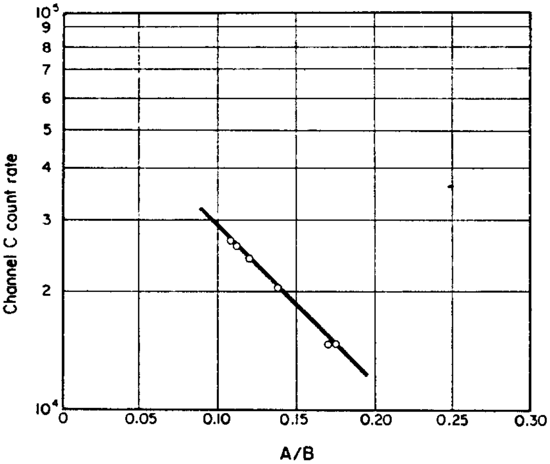

FIG. 2.—Channel *C* count rate *vs.* *A*/*B* (^{85}Kr) in presence of Rhodamine-WT.

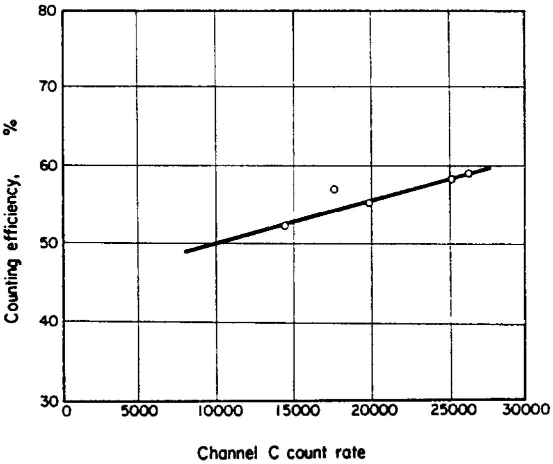

FIG. 3.—Krypton-85 counting efficiency *vs.* channel *C* count rate.

where

^{3}H = concentration of tritium in dpm present in the sample

^{85}Kr = concentration of krypton-85 in dpm present in the sample

A_{T+K} = gross count rate in channel *A* attributed to both tritium and the fraction of ^{85}Kr counts falling in that channel

B_K = gross counts in channel *B* attributed to ^{85}Kr only (tritium counts do not occur in channel *B* because of the gain and discriminator settings)

X = *A*/*B* ratio obtained from *A*/*B* *vs.* channel *C* standard curve (Fig. 2)

E_T = efficiency factor for tritium, obtained from Fig. 1

E_K = efficiency factor for krypton-85, obtained from Fig. 3.

Several replicate samples were prepared from a standard mixture of ^{3}H, ^{85}Kr, and Rhodamine-WT dye. The mixtures of sample and liquid scintillator were counted for enough time to obtain acceptable statistics for ^{3}H and ^{85}Kr. Table VIII presents the

TABLE VIII.—DETERMINATION OF ^{3}H AND ^{85}Kr IN A SINGLE SAMPLE ALIQUOT*

Channel *A, cpm*	Channel *B, cpm*	Channel *C, cpm*	^{3}H, *dpm*	^{85}Kr, *dpm*
4477	18,750	26,732	14,878	36,084
4498	18,685	25,236	14,830	36,684
4551	19,214	26,372	14,926	37,153
4485	18,724	26,853	14,973	35,976
4534	18,871	25,716	15,008	36,811
4501	19,373	27,053	14,553	37,125
4480	18,771	26,577	14,857	36,198

* Sample contained 14,850 dpm of tritium, 36,500 dpm of ^{85}Kr and 100 ppm of Rhodamine-WT dye.

gross count rate obtained in the three channels of the instrument, corrected for background, and the final calculated results for ^{3}H and ^{85}Kr, based on overall efficiencies of 14·3 and 58·4%, for ^{3}H and ^{85}Kr respectively, as derived from the standard curves.

Zusammenfassung—Zur gleichzeitigen Bestimmung von Tritium und Krypton-85 in wäßrigen Lösungen mit Flüssigkeits-Szintillationsverfahren wurden analytische Vorschriften entwickelt. Der Einfluß von Probengröße, Wassermenge und Farbstoff wurden untersucht.

Résumé—On a élaboré des méthodes analytiques pour le dosage simultané du tritium et du krypton-85 en solutions aqueuses par des techniques de scintillation liquide. On a étudié les effets de la dimension de l'échantillon, de la quantité d'eau, et des colorants.

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IDENTIFICATION OF THIOLS BY MEANS OF MERCURATED FLUORESCEIN

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Abstract—A method is proposed for the identification of thiols by examination of their complexes with tetra-acetoxymercurifluorescein (TMF). It is based on the determination of the fluorescence intensity as a function of pH and exciting wavelength, and of absorbance as a function of pH at 465 and 510 mμ. The relative fluorescence of the complexes does not depend on the wavelength of the exciting light in the range 460–500 mμ. The presence of a carboxyl group in the thiol molecule results in a strong increase of fluorescence with increasing pH and an exciting wavelength >500 mμ.

DI- AND TETRA-ACETOXYMERCURIFLUORESCEIN (DMF and TMF) give in alkaline solution a green fluorescence which is quenched by compounds containing the sulphydryl group and this reaction has been proposed as the basis for trace analysis of some sulphur compounds.[1–4] TMF has been used by Haviř *et al.*[5] for the detection of sulphur compounds on paper, by Andrew and Nichols[6] for the continuous determination of hydrogen sulphide in the atmosphere and by Yanvysheva[7] for the determination of sulphur in phosphorus. Karush *et al.*[8] have used DMF for the detection of disulphides.

A more detailed study of the idea of identifying sulphur compounds on the basis of their quenching effect on the fluorescence of TMF[4] has been undertaken in connection with a new method for the determination of the amino-acid sequence in wool. It has been shown[9] that after partial hydrolysis of wool and reduction with hydrogen selenide the resulting cysteine peptides can be separated by means of organic mercury compounds. The further work involves the resolution of the mixture into its constituents, and the determination of the structure and amino-acid composition. One approach to this is based on the examination of the TMF complexes. This method of identification of thiols in trace amounts may be valuable for investigation of certain biochemical and chemical transformations of sulphur compounds. It is essential, however, that the thiols should be completely separated from each other first, because the method applies only to characterization of individual thiols and is not applicable to their mixtures.

EXPERIMENTAL

Apparatus

Fluorimeter. Fluorescence intensity measurements were carried out with a Zeiss "Spekol" spectrophotometer equipped with a 1 × 0·8 cm cell and a TGL 10619 lamp.

Reagents

Tetra-acetoxymercurifluorescein (TMF). Prepared by White's procedure.[10] The mercury content was found by the thioglycollic procedure[8] to be 58·8%. A $5 \times 10^{-4}N$ solution of TMF was prepared by dissolution of 17·1 mg of TMF in 5 ml of $0{\cdot}1M$ sodium hydroxide, followed by dilution to 100 ml. This solution was kept for not longer than 4 days. For measurements the solution was diluted with water to $5 \times 10^{-5}N$. The diluted solution was stored in a dark flask and used within 2–10 hr of preparation.

Thio compounds. Thiols 1–8, 10–12 and 14 (see Table I) are commercially available and were generously donated by Prof. S. Veibel (Technical University of Copenhagen) and Dr. V. Chromý (Ústav Cistych Chemikalii, Brno). Acetylcysteine was prepared by the procedure of Fruton and Clarke,[11] and β-mercaptopropionamide by reaction between acrylamide and sodium disulphide, followed by reduction with hydrogen selenide.[12] The details of preparation of benzoylcysteine will be given in another paper. The cysteinylvaline was prepared from the corresponding disulphide (generously given by Dr. K. R. Harrap, Chester Beatty Research Institute, London) by reduction with hydrogen selenide.

Buffer solutions. The buffer solutions for the pH range 3·8–5·6 were prepared by mixing 0·4*M* acetic acid with 0·4*M* sodium acetate, and for pH range 5·8–7·8 by mixing 0·2*M* mono- and disodium phosphates. Decimolar solutions of borax and sodium carbonate were used for pH 9·24 and 11·1 respectively. All pH values were verified with a pH-meter after 1:1 dilution with water.

Procedure

The thiol investigated was dissolved in water, and after its concentration had been determined by titration with *o*-hydroxymercuribenzoic acid[13] it was adjusted to approx. 10^{-4} *N*. The calculated amount of this solution was added without delay to a solution containing 2 ml of buffer solution and 1 ml of $5 \times 10^{-5}N$ TMF, and the mixture was diluted to 4 ml with water. A solution of the same composition but without thiol was used as reference, and the relative fluorescence, F_r, was measured. To examine the change of fluorescence with pH a fluorescent glass was used as reference. The dependence of the fluorescence on the wavelength of excitation was determined by reference to the fluorescence of the blank at 505 mμ.

If the fluorescence altered with time, the results were extrapolated to the time of preparation of the samples.

RESULTS

Effects of the amount of thiol added

One mole of TMF is able to bind 4 sulphydryl groups, forming four Hg—S bonds. It has been found that the intensity of fluorescence decreases with increasing thiol (RSH) content in the complex until the composition TMF:RSH = 1:2 is reached and then increases again to a constant value at TMF:RSH = 1:4. Further addition of thiol has no effect on the fluorescence. The fluorescence at composition 1:2 depends on pH, excitation wavelength, and thiol used. At 500 mμ and pH 9·24 the minimum fluorescence is ~55% of that at composition 1:4. Further investigations were therefore performed with 4·4–4·8 equivalents of thiol per mole of TMF.

Effect of excitation wavelength

The influence of the excitation wavelength on fluorescence intensity at pH 11·1 is shown in Fig. 1. The maximum for the blank and the cysteamine complex is attained at 505 mμ, whereas for cysteine and glutathione the maximum is shifted to 515 mμ. The great differences in fluorescence intensity of TMF complexes can be observed. As a result of the displacement of the maximum fluorescence to the longer wavelengths, the curves for cysteine and glutathione intersect the blank curve at 527 and 519 mμ respectively. Consequently at exciting wavelengths longer than that at the point of intersection the addition of the corresponding thiol to TMF results in an increase of fluorescence. As far as could be established, this shift of maximum fluorescence is due to the presence of a dissociated carboxyl group in the thiol molecule. Moreover, the presence of such a group results in a strong increase of fluorescence (*cf.* the cysteine and cysteamine complexes).

Effect of pH

The effect of pH on the fluorescence intensity is indicated in Fig. 2. For the blank the greatest change is in the pH range 5·2–6·8. At a pH lower than 5·5 the fluorescence

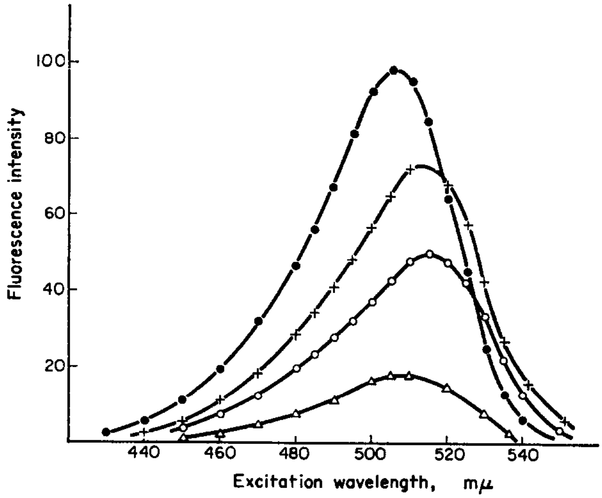

FIG. 1.—Fluorescence intensity of TMF complexes with thiols as function of the exciting wavelength.

●—TMF without thiols; ×—TMF-glutathione;
○—TMF-cysteine; △—TMF-cysteamine

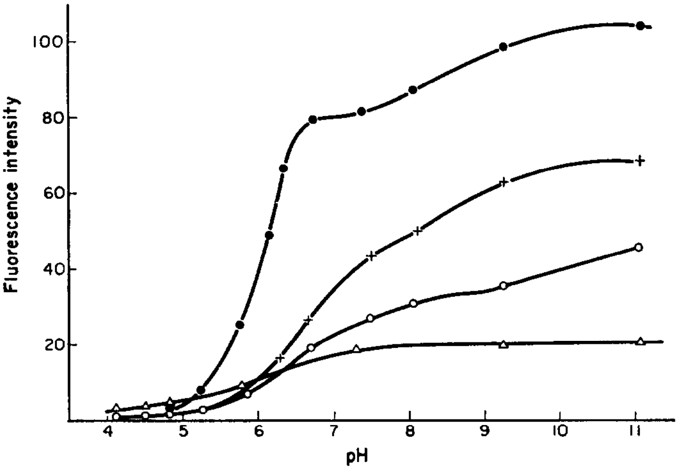

FIG. 2.—Fluorescence intensity of TMF complexes with thiols as function of pH at exciting wavelength 500 mμ.

●—TMF without thiols; ×—TMF-acetylcysteine;
○—TMF-cysteine; △—TMF-cysteamine

intensity of the cysteamine complex is greater than the fluorescence of the blank. That means that in acid solution the addition of cysteamine increases the fluorescence of the blank containing TMF. Above pH 7 the fluorescence of the cysteamine complex no longer depends on pH; however, as a result of the increase of the fluorescence of the blank reference sample the relative fluorescence decreases. The fluorescence of complexes of cysteine and acetylcysteine increases with pH over the whole range investigated.

Effect of excitation wavelength and pH on relative fluorescence

The relationship between excitation wavelength and relative fluorescence at different pH values is shown for some thiols in Figs. 3–5. The F_r values are independent of the excitation wavelength in the range 460–495 mμ for all thiols investigated, regardless of pH. The changes in the relative fluorescence as the exciting wavelengths increase beyond 500 mμ depend on the thiol and the pH, and can be divided into four classes.

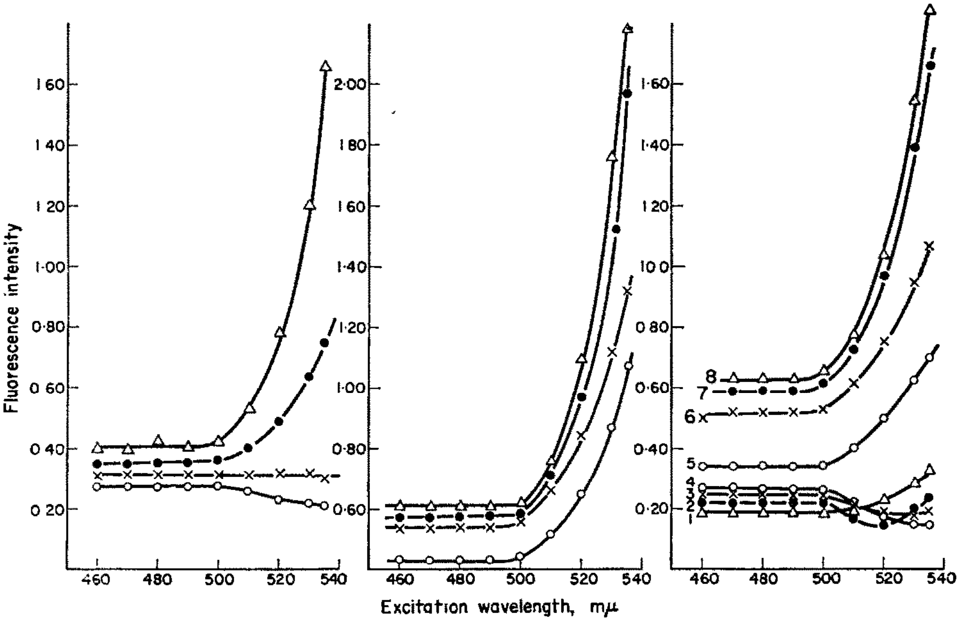

FIG. 3 FIG. 4 FIG. 5

FIG. 3.—Relative fluorescence of TMF–cysteine complex as function exciting wavelength at different pH values

○—pH 6·73; ×—pH 7·40; ●—pH 9·24; △—pH 11·1

FIG. 4.—Relative fluorescence of TMF-glutathione as function of exciting wavelength at different pH values

○—pH 6·73; ×—pH 7·40; ●—pH 9·24; △—pH 11·1

FIG. 5.—Relative fluorescence of TMF-cysteamine and TMF-acetylcysteine complexes as function of exciting wavelength at different pH.

Curves 1–4, TMF-cysteamine; curves 5–8, TMF-acetylcysteine. ○—pH 6·73; ×—pH 7·40; ●—pH 9·24; △—pH 11·1

1. Relative fluorescence does not change, *e.g.*, the complex of cysteine at pH 7·40.
2. Relative fluorescence shows a small decrease which may be followed by a small increase, *e.g.*, the complex of cysteine at pH 6·73 and of cysteamine at pH 6·73, 7·40 and 9·24.
3. Relative fluorescence shows a small increase, *e.g.*, the complex of cysteamine at pH 11·1.
4. Relative fluorescence increases strongly, *e.g.*, the complex of cysteine at pH 9·24 and 11·1, and the complexes of acetylcysteine and glutathione.

A strong increase in F_r at high pH with increasing excitation wavelength above

500 mμ indicates the presence of a carboxyl group in the thiol molecule. The influence of pH shows that the effect is due to the dissociated carboxyl group. The dissociation constant of the carboxylic group in the TMF complexes can be very different from that of the free thiol. The changes of the fluorescence with pH are very suitable for characterizing mercaptocarboxylic acids.

It is clear that the most important information can be obtained by determination of relative fluorescence in the pH range 6·7–11, at two exciting wavelengths, one below and one above 500 mμ. The wavelengths chosen were 495 and 525 mμ and the results obtained are summarized in Table I, from which some interesting conclusions can be drawn. First there is a remarkable difference between thiols containing and not containing the carboxyl group: thiols containing the carboxyl group are indicated by (1) $F_r > 0{\cdot}9$ at 11·1 and 525 mμ, (2) at pH 11·1 the ratio of the relative fluorescences at 525 and 495 mμ is $>1{\cdot}9$, (3) at 525 mμ the increase of F_r with increasing in pH from 6·73 to 11·1 is $>0{\cdot}45$; for thiols without a carboxyl group the corresponding values are (1) 0·17–0·46, (2) 0·9–1·4, (3) 0·04–0·24. On this basis the presence of the carboxyl group can easily be detected.

TABLE I.—THE RELATIVE FLUORESCENCES OF THE COMPLEXES OF TETRA-ACETOXYMERCURI-FLUORESCEIN WITH THIOLS AT VARIOUS pH VALUES AND EXCITING WAVELENGTHS, (TMF SOLUTION UNDER THE SAME CONDITIONS AS REFERENCE)

	Excitation at 495 mμ				Excitation at 525 mμ			
	pH 6·73	7·40	9·24	11·1	pH 6·73	7·40	9·24	11·1
1. Methyl mercaptan	0·20	0·30	0·28	0·26	0·12	0·20	0·30	0·25
2. *β*-Mercaptoethanol	0·09	0·14	0·21	0·18	0·05	0·08	0·19	0·17
3. Cysteamine	0·26	0·24	0·20	0·19	0·17	0·16	0·16	0·24
4. Thioglycollic acid	0·25	0·42	0·55	0·56	0·40	0·70	1·10	1·13
5. *β*-Mercaptopropionic acid	0·21	0·33	0·53	0·54	0·24	0·44	1·02	1·04
6. Thiomalic acid	0·16	0·30	0·53	0·53	0·19	0·48	1·14	1·16
7. Thioglucose	0·34	0·40	0·41	0·34	0·35	0·42	0·54	0·39
8. Thioglycollamide	0·29	0·33	0·34	0·30	0·28	0·32	0·39	0·34
9. *β*-Mercaptopropionamide	0·23	0·28	0·32	0·33	0·22	0·26	0·41	0·46
10. Penicillamine	0·25	0·33	0·46	0·41	0·27	0·40	1·09	1·22
11. Homocysteine	0·23	0·24	0·24	0·48	0·17	0·19	0·23	0·94
12. Cysteine	0·27	0·31	0·35	0·41	0·22	0·31	0·54	0·98
13. *N*-Acetylcysteine	0·34	0·51	0·60	0·62	0·55	0·85	1·16	1·28
14. *N*-Benzoylcysteine	0·27	0·38	0·40	0·39	0·87	1·17	1·43	1·30
15. Cysteinylvaline	0·37	0·36	0·47	0·47	0·49	0·47	1·05	1·10
16. Gultathione	0·44	0·54	0·58	0·61	0·77	1·00	1·24	1·35

The conversion of the carboxyl into the amide group exerts a small effect at low pH and 495 mμ, and a very strong one at high pH and 525 mμ. The differences in F_r for various thiols depend on pH and exciting wavelength. In order to ascertain which of the known thiols is present in the sample, the conditions corresponding to the greatest differences of F_r values should be chosen, *e.g.*, the most favourable conditions to decide between cysteine, homocysteine and pencillamine are at 525 mμ and pH 9·24.

Ethyl-, n-butyl- and benzylmercaptan and *p*-thiocresol in the form of the TMF complexes give at pH 9·24 F_r values of 0·24, 0·21, 0·13 and 0·08. There is no distinct influence of exciting wavelength on these values.

Characterization of thiols from pH–absorbance curves

Although the F_r values are sufficient for characterizing and identifying many thiols, additional information is required for confirmation. This can be obtained from absorbance measurements at various pH. Complexes of TMF with thiols are yellow in acid solution and red to pinkish orange in alkaline solution, the change of the colour with pH being reversible. The maximum absorption of the yellow complex occurs at 465 mμ and of the red one at 510 mμ. With increasing pH the absorbance at 465 mμ decreases and at 510 mμ increases, the curves intersecting at a pH value characteristic of the thiol concerned. This pH may be called the conversion point.

Procedure. To the solution containing 2 ml of buffer and 2 ml of $5 \times 10^{-5}N$ TMF add the thiol in excess (<1 ml), dilute to 5 ml, and measure the absorbance at 465 and 510 mμ in a 1-cm cell. Repeat for various pH values and find the conversion point graphically.

Some results found by this procedure, Table II, show that the conversion points increase in general with increasing acidity of the thiols, from 5·23 for cysteamine to 7·00 for thiomalic acid. Although these conversion points have no distinct physical meaning they can be used as an additional characteristic of thiols. The complexes of thiols such as methyl-, ethyl- and phenylmercaptan change colour from orange in acid solution to red in alkaline solution and cannot be identified by the procedure given above.

TABLE II.—THE pH VALUES (CONVERSION POINTS) CORRESPONDING TO EQUAL ABSORBANCE AT 465 mμ AND 510 mμ OF THE TMF–THIOL COMPLEXES

Thiol	pH
Cysteamine	5·23
Thioglucose	5·80
Glutathione	6·15
Cysteine	6·35
β-Mercaptoethanol	6·35
β-Mercaptopropanamide	6·40
Thioglicollic acid	6·50
β-Mercaptopropionic acid	6·70
Thiomalic acid	7·00

On the basis of the results described in this paper the TMF method appears to be very suitable for identification of thiols. For this purpose the relative fluorescence should be determined under the conditions given in Table I. If the thiol which is supposed to be present in the sample is available, the measurements can be repeated with TMF complex of the known thiol as reference. If the relative fluorescences found in this way are equal the identity can be considered as proved. Only a single thiol must be present in the sample.

Zusammenfassung—Es wird vorgeschlagen, Thiole durch Untersuchung ihrer Komplexe mit Tetraacetoxymercurifluorescein (TMF) zu identifizieren. Das beruht auf der Bestimmung der Fluoreszenzintensität als Funktion von pH und Anregungswellenlänge sowie der Absorption als Funktion des pH bei 465 und 510 nm. Die relative Fluoreszenz der Komplexe hängt im Bereich 460–500 nm nicht von der Anregungswellenlänge ab. Eine Carboxylgruppe im Thiolmolekül ergibt ein starkes Ansteigen der Fluoresenz bei steigendem pH und einer Anregungswellenlänge über 500 nm.

Résumé—On propose une méthode pour l'identification des thiols par examen de leurs complexes avec la tétra-acétoxymercurifluorescéine (TMF). Elle est basée sur la détermination de l'intensité de fluorescence en fonction du pH et de la longueur d'onde d'excitation, et de l'absorption en fonction du pH à 465 et 510 mμ. La fluorescence relative des complexes ne dépend pas de la longueur d'onde de la lumière excitatrice dans le domaine 460–500 mμ. La présence d'un groupement carboxylique dans la molécule de thiol a pour conséquence un fort accroissement de la fluorescence lorsque le pH croît, et une longueur d'onde excitatrice > 500 mμ.

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EXTRACTION OF CERTAIN ELEMENTS FROM AQUEOUS METHANOL, ETHANOL AND ACETONE BY TRIDODECYLAMINE AND TRIBUTYL PHOSPHATE

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Summary—The extraction of silver, mercury, selenium, zinc, cobalt and iron with tridodecylamine (TDA) and tributyl phosphate (TBP) from hydrochloric acid solutions in aqueous methanol, ethanol and acetone is reported. The presence of these additives increases extraction for some elements and decreases it for others. The effect is generally greater with TDA than with TBP.

IN A previous paper[1] the extraction of antimony with tertiary amines from various acidic media was reported; when methanol, ethanol or acetone was added to aqueous hydrochloric acid solutions, the extraction of antimony was enhanced considerably. This increase has been interpreted as due to the decrease in hydration as the mole fraction of water decreases, which in turn brings about an increase in the formation of extractable antimony complexes.

In the present communication the work is extended to some other elements, which on irradiation give rise to long-lived radioisotopes. The separation of such radioisotopes is often required, *e.g.*, in activation or isotope dilution analysis. Results on the extraction of silver, mercury(II), selenium(IV), zinc, cobalt(II) and iron(III) with tridodecylamine (TDA) and tributyl phosphate (TBP) are presented.

EXPERIMENTAL

Apparatus

As described before.[1]

Reagents

Solutions of TDA and TBP were prepared by dissolving the appropriate amounts in reagent-grade xylene. Other reagents were prepared from analytical-grade chemicals.

^{110}Ag, ^{203}Hg, ^{75}Se, ^{65}Zn, ^{60}Co and ^{59}Fe were used as tracers and were prepared as described elsewhere.[2]

Procedure

Extraction experiments were performed in the usual way[1] and the distribution coefficient (E) was taken to be the ratio of the activities of the tracer in the organic and aqueous phases. Determinations were carried out only in duplicate, because of the high reproducibility of the results. Microgram or tracer amounts of the elements were used, and equal volumes (usually 10 ml) of the organic and aqueous phases.

RESULTS AND DISCUSSION

The behaviour of the elements in the presence of organic additives can generally be explained in terms of the known mechanisms for TDA and TBP extraction:[3–7]

$$m\text{TDAHCl} + \text{MCl}_{m+n}^{m-} \rightleftharpoons (\text{TDAH})_m\cdot\text{MCl}_{m+n} + m\text{Cl}^- \qquad (1)$$

$$m\text{TBP} + \text{M}^{n+} + n\text{Cl}^- \rightleftharpoons (\text{TBP})_m\cdot\text{MCl}_n. \qquad (2)$$

Although other mechanisms have been proposed,[5] it is not within the scope of this paper to prove which of the alternatives occurs.

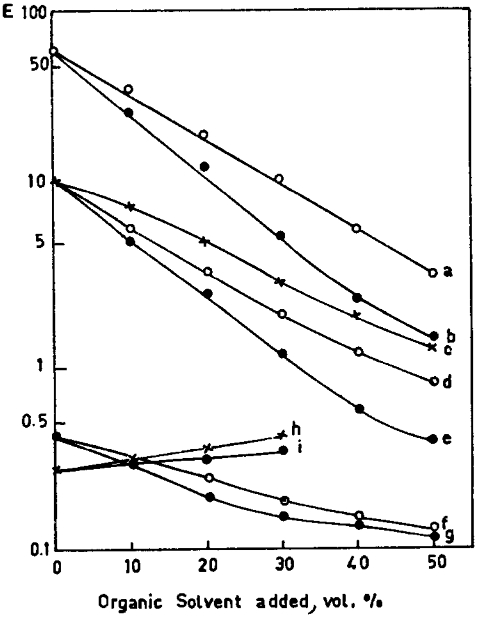

FIG. 1.—Effect of organic additives on *E* for Ag.
a—methanol in 0·5*M* HCl; 0·06*M* TDA
b—ethanol in 0·5*M* HCl; 0·06*M* TDA
c—acetone in 1·5*M* HCl; 0·06*M* TDA
d—methanol in 1·5*M* HCl; 0·06*M* TDA
e—ethanol in 1·5*M* HCl; 0·06*M* TDA
f—methanol in 6*M* HCl; 0·06*M* TDA
g—ethanol in 6*M* HCl; 0·06*M* TDA
h—ethanol in 6*M* HCl; 50% TBP
i—methanol in 6*M* HCl; 50% TBP

Data on the extraction of silver with 0·06*M* TDA from 0·5, 1·5 and 6*M* hydrochloric acid (Fig. 1 curves a–g) show that, contrary to the behaviour in the antimony extraction, *E* for silver decreases with increase in the organic solvent concentration; the effect becomes more marked in the order acetone < methanol < ethanol. Thus the value of *E* decreases from 11·5 in 1·5*M* hydrochloric acid to 0·3 when 1·5*M* hydrochloric acid in 50% v/v aqueous ethanol is used.

On the other hand *E* for silver increases slightly with increasing concentration of organic additive in the TBP extraction (Fig. 1 curves h and i). This confirms that the mechanism of silver extraction with TBP is different from that with TDA. The decrease in TDA extraction of silver is possibly due to competition between HCl_2^- and

$AgCl_2^-$ for the protonated amine $TDAH^+$; the formation of the amine dichloride ($TDAH^+ \cdot HCl_2^-$) has been confirmed by many authors.[3–5] The value of *E* for silver therefore decreases in the presence of organic additives as well as with increase in the concentration of hydrochloric acid itself in the absence of organic solvents (Table I).

TABLE I.—EFFECT OF METHANOL ON TDA EXTRACTION OF SILVER AND MERCURY IN THE PRESENCE OF VARIOUS CONCENTRATIONS OF HYDROCHLORIC ACID

Original [HCl] in aqueous phase, *M*	Methanol in aqueous phase, % v/v	*E*	
		Ag	Hg
0·5	0	60	—
1·5		11·16	77
1·8		8·13	69
2·1		6·75	54
2·4		4·42	57
2·7		3·85	59
2·85		3·27	63
0·5	5	47	—
1·5		8·5	62
2·85		2·85	52·7
6·0		0·37	—
0·5	10	37·5	—
1·5		6·2	51·0
2·7		2·42	38·5
6·0		0·32	—
0·5	20	20·5	—
1·5		3·5	32·0
2·4		1·73	21·0
6·0		0·25	—
0·5	30	11·5	—
1·5		2·0	20·5
2·1		1·34	17·6
6·0		0·19	—
0·5	40	6·0	—
1·5		1·3	11·3
1·8		1·03	10·3
6·0		0·15	—
0·5	50	3·5	—
1·5		0·8	6·09
6·0		0·12	—

The presence of organic additives also brings about a considerable decrease of *E* for mercury extraction with TDA, but only a very slight decrease of *E* for extraction with TBP (Fig. 2 and Table I). The behaviour of mercury can be explained in the same way as for silver.

Selenium extraction with both TDA and TBP increases at first slowly and then sharply with increasing concentration of organic additive (Fig. 3). The behaviour of zinc (Fig. 4) is very similar to that of mercury.

The effect on the extraction of cobalt increases in the order water < methanol < ethanol < acetone with either TDA or TBP. Thus the value of *E* for cobalt extraction

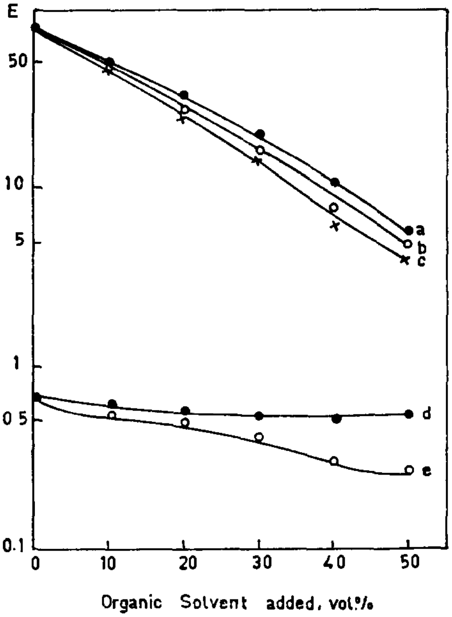

FIG. 2.—Effect of organic additives on E for Hg.
a—acetone in 1·5M HCl; 0·06M TDA
b—methanol in 1·5M HCl; 0·06M TDA
c—ethanol in 1·5M HCl; 0·06M TDA
d—ethanol in 1·5M HCl; 50% TBP
e—methanol in 1·5M HCl; 50% TBP

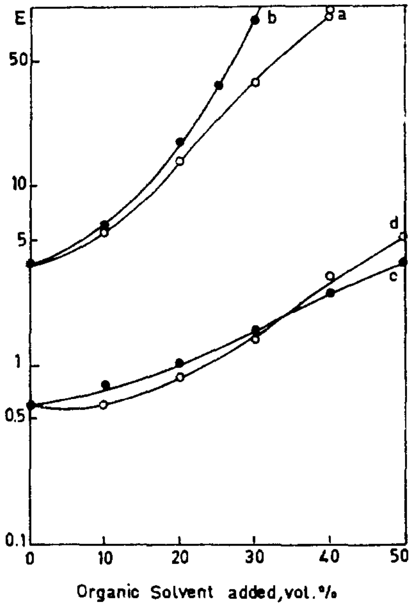

FIG. 3.—Effect of organic additives on E for selenium.
a—methanol in 6M HCl; 0·06M TDA
b—ethanol in 6M HCl; 0·06M TDA
c—methanol in 6M HCl; 50% TBP
d—ethanol in 6M HCl; 50% TBP

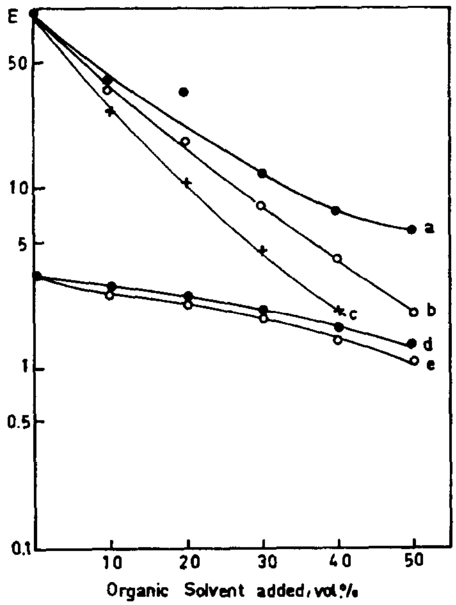

FIG. 4.—Effect of organic additives on *E* for zinc.
a—acetone in 1·5*M* HCl; 0·06*M* TDA
b—methanol in 1·5*M* HCl; 0·06*M* TDA
c—ethanol in 1·5*M* HCl; 0·06*M* TDA
d—ethanol in 6*M* HCl; 50% TBP
e—methanol in 6*M* HCl; 50% TBP

with TBP increases from less than 0·1 in pure aqueous 6*M* hydrochloric acid to more than 1 in 6*M* hydrochloric acid in 50% v/v aqueous ethanol (Fig. 5).

The extraction of iron is only slightly affected by the presence of organic additives. It decreases for TDA and increases for TBP (Fig. 6), the slight change in the case of TDA extraction is due to cancellation of the two opposing effects; the decrease in hydration leads to an increase in extraction and the formation of amine dichloride leads to a decrease.

Applications

Both silver and mercury are highly extractable and cannot be separated from each other in pure aqueous hydrochloric acid solutions of low acidity; from 1·5*M* hydrochloric acid the respective *E* values are 11·2 and 77 for extraction with 0·06*M* TDA. On the other hand, the corresponding *E* values for 1·5*M* hydrochloric acid in 50% v/v aqueous ethanol are 0·3 and 4·0. Accordingly the two elements may be easily separated by the selective extraction of mercury with the latter extraction system. Alternatively silver and mercury, which are co-extracted with TDA from pure aqueous hydrochloric acid solutions may be easily separated by the selective stripping of silver from TDA by 1·5*M* hydrochloric in 50% aqueous ethanol. This is more convenient than stripping with concentrated hydrochloric acid[8] for obvious reasons.

Selenium can be separated from silver by extraction with 0·06*M* TDA from 1·5*M* hydrochloric acid in 50% aqueous ethanol and from both silver and mercury

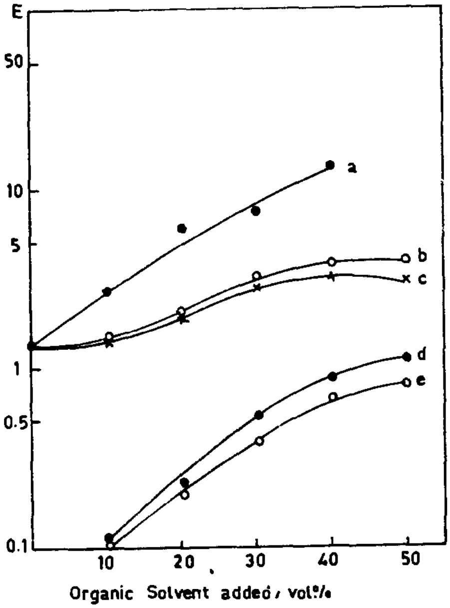

FIG. 5.—Effect of organic additives on *E* for cobalt.
a—acetone in 6*M* HCl; 0·06*M* TDA
b—ethanol in 6*M* HCl; 0·06*M* TDA
c—methanol in 6*M* HCl; 0·06*M* TDA
d—ethanol in 6*M* HCl; 50% TBP
e—methanol in 6*M* HCl; 50% TBP

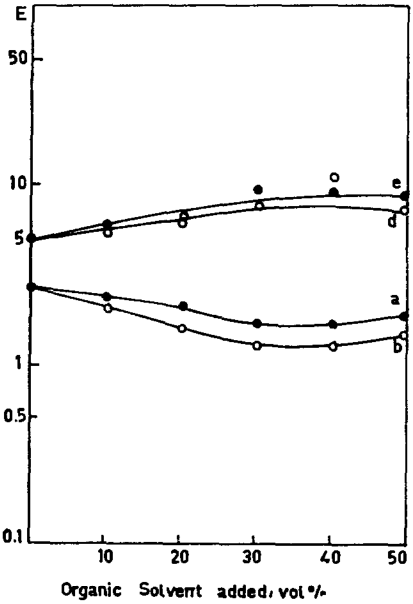

FIG. 6.—Effect of organic additives on *E* for iron.
a—methanol in 1·5*M* HCl; 0·06*M* TDA
b—ethanol in 1·5*M* HCl; 0·06*M* TDA
c—ethanol in 6*M* HCl; 50% TBP
d—methanol in 6*M* HCl; 50% TBP

by extraction with 50% TBP from 1·5*M* hydrochloric acid in 50% aqueous methanol. Such separations cannot be achieved from pure aqueous solutions.

Conclusion

The reported data are concerned with submilligram amounts of the studied elements, which is of special interest in working up elaborate radiochemical separation procedures. It would also be valuable to study the extraction of macro (gram) amounts of these elements in the presence of water-miscible organic additives, and to investigate more widely the nature of the extraction mechanism. The work can also be extended to other elements and to other solvents which form ion-association complexes in the organic phase.

Zusammenfassung—Es wird über die Extraktion von Silber, Quecksilber, Selen, Zink, Kobalt und Eisen mit Tridodecylamin (TDA) und Tributylphosphat (TBP) aus salzsauren Lösungen in wäßrigem Methanol, Äthanol und Aceton berichtet. Die Gegenwart dieser Zusätze verbessert die Extraktion einiger Elemente und vermindert sie bei anderen. Bei TDA ist der Effekt im allgemeinen größer als bei TBP.

Résumé—On décrit l'extraction de l'argent, du mercure, du sélénium, du zinc, du cobalt et du fer au moyen de tridodécylamine (TDA) et de tributylphosphate (TBP) à partir de solutions dans l'acide chlorhydrique en méthanol, éthanol et acétone aqueux. La présence de ces additifs accroît l'extraction puor quelques éléments et l'abaisse pour d'autres l'effet est généralement plus important avec TDA qu'avec TBP.

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SHORT COMMUNICATIONS

Neutron Activation Analysis by Standard Addition and Solvent Extraction. Determination of Impurities in Thorium and Iron

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In a previous paper[1] a separation scheme was described for the simultaneous determination of scandium, cobalt, iron, zinc, silver, mercury, chromium and rubidium in aluminium by neutron activation analysis. The induced ^{60}Co, ^{59}Fe, ^{65}Zn, ^{110}Ag and ^{203}Hg are fractionated by tridodecylamine (TDA) extraction. The induced ^{46}Sc is extracted with tributylphosphate (TBP), while ^{51}Cr and ^{86}Rb are determined in the aqueous solution by gamma-ray spectrometry. ^{233}Pa which is obtained in one of the fractions was shown in another paper[2] to be separated from ^{60}Co by extraction with thenoyltrifluoroacetone (TTA), thus allowing the determination of thorium in aluminium.

In the present communication studies have been performed in order to improve the separation procedure and to make it suitable for the determination of trace elements in thorium and iron.

EXPERIMENTAL

Studies on the extractability of ^{110}Ag, ^{65}Zn and ^{203}Hg with 0·3*M* TDA have shown that the degrees of extraction of the three radionuclides from 12*M* hydrochloric acid are 1, 97 and 99% respectively. Accordingly ^{110}Ag can be stripped with 12*M* hydrochloric acid from the TDA extract before the elution of ^{65}Zn with 1*M* nitric acid; this makes possible the determination of silver and mercury in separate fractions.

Determination of impurities in thorium nitrate

Elements present in trace amounts in thorium affect its physical metallurgy and the neutron economy in the "breeding" reaction:

$$^{232}\text{Th}(n, \gamma)^{233}\text{Th} \xrightarrow[23\cdot5\ \text{min}]{\beta^-} {}^{233}\text{Pa} \xrightarrow[27\ \text{d}]{\beta^-} {}^{233}\text{U} \qquad (1)$$

Methods for the determination of trace elements in thorium have been developed.[3] Emission spectroscopic methods have been widely used for the determination of many impurities in thorium,[4] while chemical methods, because of their greater accuracy, are sometimes of major importance.[5-10]

The application of neutron-activation methods to the determination of impurities in thorium and its concentrates is difficult, owing to the very high activity induced from thorium as a result of neutron irradiation. Thus, as can be seen from reaction (1) difficulties will be met with in the determination of impurities giving rise to both short and long-lived radioisotopes. Methods of separation which would give high decontamination factors from activated matrix components should therefore be applied, since no cooling can be allowed.

Samples of thorium nitrate (about 250 mg) are wrapped in thin aluminium foils. For quantitative analysis, the samples and standards are placed together in an aluminium can and irradiated as described previously.[1]

Each thorium sample is carefully removed from the aluminium foil, transferred to a 100-ml beaker and subsequently dissolved in 1·3*M* hydrochloric acid. The foil is washed with the minimium quantity of 1*M* nitric acid. The solution is then transferred to a 25-ml graduated flask, the inside walls of the beaker being washed with 1·3*M* hydrochloric acid, and then made up to the mark with 1·3*M* hydrochloric acid. The extraction of ^{233}Pa with TTA[2,11] is applied for its separation from other nuclides.

By two successive extractions with 0·5*M* TTA in xylene, ^{233}Pa (together with ^{95}Zr) is almost completely removed from the irradiated thorium solution. The volumes of organic and aqueous phase used are in 2:1 ratio. About 60% of ^{59}Fe together with major proportions of the other radionuclides remain in the aqueous phase. Owing to the very high activity of the induced ^{233}Pa, shaking should not be done by hand but on a suitably shielded mechanical shaker. The time required for reaching extraction equilibrium with TTA on the shaker is about 15 min.

The thorium solution is then made 6*M* in lithium chloride and 3*M* in hydrochloric acid; the extractability of isotopes from this medium with 0·3*M* TDA is similar to their extractability from 2·5*M* aluminium chloride–1·5*M* hydrochloric acid. In other words cobalt, niobium, iron, silver, zinc and mercury can be extracted with 0·3*M* TDA from 6*M* lithium chloride–3*M* hydrochloric acid, while scandium, chromium, rare earths and rubidium remain in the aqueous phase. Traces of protactinium (which may be left after extraction with TTA) will also be extracted from this medium. Fractions containing cobalt, iron, silver and zinc are therefore contaminated with traces of ^{233}Pa. The possibility of eliminating ^{233}Pa by another extraction with TTA has been considered. The extractability of ^{233}Pa and the other isotopes with TTA from various media is shown in Table I.

TABLE I.—EXTRACTION OF ^{233}Pa AND OTHER ISOTOPES WITH 0·5*M* TTA

Medium	Isotope	Extraction, %
1·7*M* HCl	^{233}Pa	99
	^{60}Co	0·1
	^{233}Pa	0·1
3*M* HF–0·5*M* HCl	^{59}Fe	—
12*M* HCl	^{233}Pa	79
	^{110}Ag	0·1
1*M* HNO$_3$	^{233}Pa	96
	^{65}Zn	0·1

It can be seen that the 1·7*M* hydrochloric acid, 12*M* hydrochloric acid and 1*M* nitric acid fractions can be partly freed from ^{233}Pa by one or two extractions with TTA. Recovery values greater than 50% for iron and 80% for the other isotopes are obtainable, while satisfactory reproducibility of separation is achieved.

When the modified separation scheme was applied to an irradiated sample solution of analytical reagent grade thorium nitrate none of the impurities listed above were detected, and only zirconium was identified (*via* ^{95}Nb) in an "Indian Nuclear Pure" sample (Fig. 1*b*). For testing the scheme, irradiated thorium nitrate was mixed with varying amounts of irradiated standard solutions. Typical

TABLE II.—ANALYSIS OF IMPURITIES IN THORIUM NITRATE (50 mg)

Element	Nuclide identified*	Half-life	Amount added (as metal), *ppm*	Photopeak activity, *cpm* A†	Photopeak activity, *cpm* A$_m$†	Amount found, *ppm*
			—	—	1934	b.d‡
Scandium	^{46}Sc(1·12)	85d	1	2104	4008	1·1
			2	4217	5929	2·48
			—	—	975	b.d.
Cobalt	^{60}Co(1·33)	5·3y	10	1199	2571	8·7
			20	2286	3353	21·6
			—	—	77	b.d.
Iron	^{59}Fe(1·10)	45d	100	69	124	124
			200	138	200	220
			—	—	92	b.d.
Zinc	^{65}Zn(1·11)	245d	30	90	208	23·0
			60	183	277	58·0
			—	—	426	b.d.
Mercury	^{203}Hg(0·28)	458d	2	502	923	2·38
			4	1026	1391	5·80

* In brackets are given the energies of the photopeaks in (MeV) used for quantitative analysis.

† See reference 1.

‡ b.d. = beyond detection.

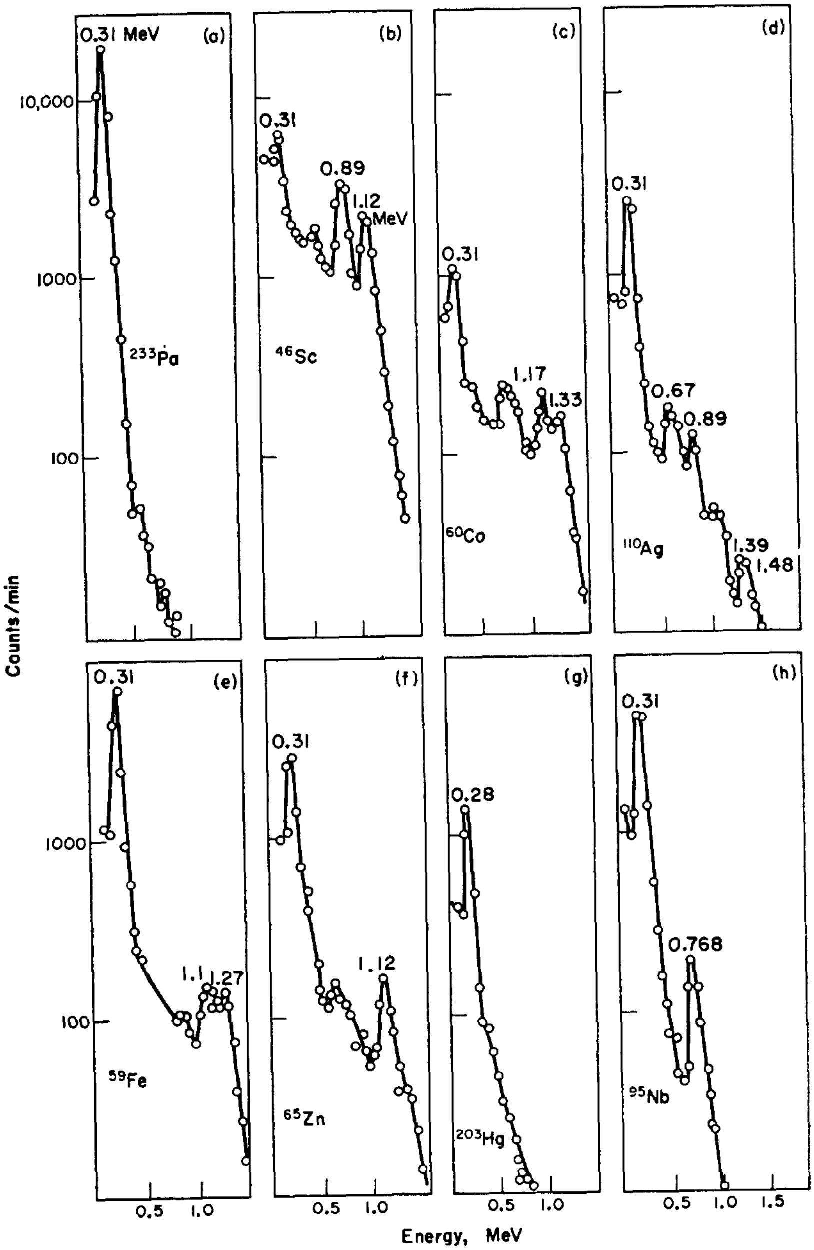

FIG. 1.—Gamma-ray spectra.

a—Irradiated thorium solution.
b—TBP extract.
c—1·7*M* HCl strip solution.
d—12*M* HCl strip solution.
e—3*M* HF–0·5*M* HCl strip solution.
f—1*M* HNO_3 strip solution.
g—Final TDA extract.
h—1·7*M* HCl strip solution from Indian thorium.

TABLE III.—EXTRACTION OF RADIOISOTOPES WITH ISOPROPYL ETHER FROM 9*M* HCl

Isotope	Extraction, %
^{59}Fe	99·9 (99·9)*
^{233}Pa	<1·0
^{60}Co	<1·0 (0)*
^{110}Ag	<1·0
^{65}Zn	<1·0 (19·5)*
^{203}Hg	<1·0
^{46}Sc	<1·0 (0)*
^{51}Cr	<1·0
^{134}Cs	<1·0
^{86}Rb	<1·0
^{141}Ce(III)	<1·0

* These values in brackets have been reported in a previous paper.[16]

gamma-spectra of the artificially contaminated thorium solution and of the isolated fractions are shown in Fig. 1. It is clear that ^{233}Pa contaminates ^{46}Sc, ^{60}Co, ^{59}Fe, ^{110}Ag and ^{65}Zn, while ^{203}Hg is very pure. The incomplete decontamination from ^{233}Pa can be explained by the presence of a small amount of inextractable material.[12] ^{60}Co is also contaminated with ^{95}Nb. Fortunately ^{233}Pa and ^{95}Nb are less active, and their presence does not represent any difficulty in the analysis of these nuclides. ^{95}Nb may be separated from cobalt by extraction with tribenzylamine from 11*M* hydrochloric acid[13] or with a secondary amine,[14] thus allowing the determination of zirconium in thorium. In this case analysis should be carried out at least a month after irradiation, to allow for the growth of ^{95}Nb.

The results of quantitative analysis carried out as described[1,15] on artificially contaminated thorium samples are presented in Table II. There was satisfactory agreement between the amount added and the amount found for all the elements.

TABLE IV.—ANALYSIS OF IMPURITIES IN IRON OXIDE (50 mg)

Element*	Amount added (as metal), *ppm*	Amount found,‡ *ppm*
	—	b.d
Scandium	1	1·06
	2	2·12
	—	b.d.
Cobalt	5	4·31
	10	9·53
	—	—
Thorium†	2	1·74
	4	3·85
	—	b.d.
Silver	2	2·6
	—	b.d.
Zinc	60	71·0
	120	105·0
	—	—
Mercury	4	3·69

* For the induced isotopes and energies of photopeaks used for quantitative analysis see Table II.

† Determined by counting the 0·31 MeV peak activity of ^{233}Pa.

‡ Average of two determinations, b.d. = beyond detection.

Determination of impurities in iron

The determination of impurities in iron by neutron activation analysis has been reported in a recent paper.[16] Nondestructive methods have been applied for some elements, while radiochemical separation procedures using ion-exchange chromatography and solvent extraction techniques have been used for others. A preliminary removal of the induced ^{59}Fe has been performed by extraction with isopropyl ether.

In this study the improved separation scheme has been applied for the determination of impurities in iron, after a preliminary separation of ^{59}Fe with isopropyl ether.[16]

In Table III are presented our data on the extraction of iron and the other induced radioisotopes, from $9M$ hydrochloric acid; it is clear that only iron is quantitatively extracted, while the other isotopes remain in the aqueous layer. The aqueous solution is then made $6M$ in lithium chloride and $3M$ in hydrochloric acid and the induced radionuclides are subsequently fractionated as described before.[1,2] ^{51}Cr which is obtained in the final aqueous phase together with the isotopes induced from alkali metals, alkaline earths and rare earths can be separated by extraction with tribenzylamine.[16]

Results obtained on artificially contaminated iron samples show that ^{46}Sc, ^{60}Co, ^{233}Pa, ^{110}Ag, ^{65}Zn and ^{203}Hg are separated in a pure form, so that analysis can also be performed using simple counters without appreciable increase in the error.

For quantitative analysis samples of ferrous materials are placed together with standards in an aluminium can for pile irradiation.[1] The results of quantitative analysis carried out as usual,[1,15] on artificially contaminated iron samples, are shown in Table IV. Satisfactory agreement is obtained between the amount of element added and the amount found.

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Summary—The neutron activation analysis of trace impurities in thorium nitrate and in iron is facilitated by solvent extraction procedures prior to counting.

Zusammenfassung—Die Neutronenaktivierungsanalyse von Spurenverunreinigungen in Thoriumnitrat und in Eisen wird durch Solventextraktionsschritte vor dem Zählen erleichtert.

Résumé—L'analyse par activation de neutrons de traces d'impuretés dans le nitrate de thorium et dans le fer est facilitée par des techniques d'extraction par solvant avant comptage.

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Neutron-activation analysis by standard addition and solvent extraction. Determination of traces of antimony

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NEUTRON-ACTIVATION analysis by standard addition and solvent extraction[1] was found to be suitable for the determination of elements such as uranium[2] and thorium[3] which on irradiation give rise to nuclides which have no stable isotopic carriers. In the simultaneous determination of many trace elements by this technique the induced radioisotopes could be separated much more rapidly than by the usual methods.[4,5]

In this communication the method is applied to the determination of traces of antimony. Although the degree of extraction of antimony(III) and (V) chlorides with amines is very high,[6] removal of all interfering ions by either scrubbing or stripping could not be realized. Of the other possible solvents, isopropyl ether,[7] hexone[8] and tributyl phosphate (TBP)[9] could be applied in different procedures for the radiochemical purification of antimony.

EXPERIMENTAL

Reagents

Solvents. Isopropyl ether and hexone were used without further purification. TBP was purified by washing with 5% sodium carbonate solution and then with water. TBP was used as a 50% v/v solution in xylene.

Antimony carrier solution. Antimony(V) solution (0·144*M* in 6*M* hydrochloric acid) was prepared as described before.[6]

Tracers. ^{72}Ga was prepared by dissolving irradiated gallium chloride in 6*M* hydrochloric acid. ^{76}As was prepared by dissolving irradiated specpure arsenic(III) oxide in hydrochloric acid. Other tracers were prepared as described elsewhere.[2-8]

Other reagents were prepared from high purity chemicals. The apparatus has been described previously.[4]

Preliminary studies

The extractability of antimony and other ions was examined as follows. Five ml of acid of the desired molarity were placed in a separatory-funnel and 50 μl of tracer solution were added. The solution was shaken with 5 ml of solvent until equilibrium was attained (4–5 min for isopropyl ether; 30 sec for hexone or TBP). The phases were separated and various scrubbing agents tested. The activities of equal volumes (3·0 ml) of the organic and aqueous phases were then measured.

The degree of extraction from the media finally selected for separation is shown in Table I.

TABLE I.—EXTRACTION OF ^{124}Sb AND OTHER ISOTOPES WITH VARIOUS SOLVENTS

Isotope	Extraction, %					
	Isopropyl ether		Hexone		50% TBP in xylene	
	6*M* HCl	1·5*M* HCl	6*M* HCl	0·1*M* HCl	4*M* HCl 4*M* LiCl	1*M* HNO_3
^{124}Sb(V)	>99	73	98·5	<1·0	>99	<1·0
^{124}Sb(III)	3	—	79	<1·0	>99	<1·0
^{46}Sc	<1·0	—	<1·0	—	94	<1·0
^{60}Co	<1·0	—	<1·0	—	61	<1·0
^{65}Zn	<1·0	—	<1·0	—	95	<1·0
^{72}Ga	94	<1·0	99	<1·0	>99	<1·0
^{59}Fe(III)	55·5	2·0	61	<1·0	>99	<1·0
^{76}As(V)	1·5	—	82	<1·0	71	6
^{203}Hg(II)	<1·0	—	23	<1·0	83	10
^{110}Ag	<1·0	—	2·5	—	85	<1·0
^{51}Cr(III)	<1·0	—	<1·0	—	1·5	<1·0
^{134}Cs	<1·0	—	<1·0	—	<1·0	—
^{86}Rb	<1·0	—	<1·0	—	<1·0	—

It is clear from these results that in order to increase the separation yield in isopropyl ether and hexone extraction, antimony should be oxidized to antimony(V), for example by the addition of concentrated nitric acid during the dissolution procedure or by the addition of other oxidizing agents such as bromine water or potassium bromate solution.

The extraction of antimony(V) and many other ions from $6M$ hydrochloric acid with hexone and from $4M$ hydrochloric acid–$4M$ lithium chloride with TBP is seen to be very efficient. At low acidities ($0{\cdot}1M$ hydrochloric acid in the case of hexone and $1M$ nitric acid in the case of TBP) extraction of all ions, including antimony(V), is very poor. However when the hexone or TBP solutions are stripped with an aqueous solution of the same acidity, antimony(V) is retained in the organic phase (92% in hexone and 80% in TBP) while all other ions pass into the aqueous phase. The behaviour of antimony is possibly due to the formation of certain extractable antimony species in strongly acidic solutions; such species are not formed at low acidities. The rates of formation and decomposition of these species result in roughly equal extraction and back-extraction rates. Thus kinetic experiments (Table II) show that the rate constant of antimony back-extraction is so small that the amount of the element which passes into the aqueous phase does not increase even after 15 min shaking. The examination of longer extraction periods would be interesting, but is beyond the scope of the present work.

TABLE II.—EFFECT OF TIME ON EXTRACTION OF Sb(V) FROM $0{\cdot}1M$ HCl WITH HEXONE

Shaking time, *min*	% Sb in the aqueous phase	
	Forward extraction	Back-extraction
0·1	>99	6·5
0·5	>99	8·3
1	>99	8·1
2	>99	8·2
4	>99	8·4
8	>99	8·5
15	>99	8·3

The reproducibility of separation was investigated by extracting increasing amounts (50–250 μl) of ^{124}Sb tracer as described under *Procedure* and then measuring the radioactivity of 3·0 ml of the final organic extracts. The results were found to vary by not more than a few per cent when an antimony carrier was used; the discrepancies increased in the absence of a carrier. In general, reproducibility is higher with hexone and TBP than with isopropyl ether. Yields $>$ 60, 90 and 75% were obtained for isopropyl ether, hexone and TBP extraction, respectively.

Removal of interfering ions

In the isopropyl ether extraction from $6M$ hydrochloric acid, iron and gallium can be removed from the extract by scrubbing with $1{\cdot}5M$ hydrochloric acid, but about 25% of the antimony is also back-extracted and the reproducibility is poor unless a carrier is added. In the hexone and TBP extractions it is best to take advantage of the kinetic effect on antimony back-extraction, and to perform the initial extraction from highly acidic medium, followed by scrubbing the solution with a less acidic solution. The yield of antimony is thereby somewhat reduced, but interfering elements are removed.

Procedure

Irradiation. Duplicate samples of metallic aluminium taken from cans used for pile irradiation, standard rock W-1, and coin (an Egyptian piastre made from an aluminium–magnesium alloy) were packed in thin aluminium foil and irradiated in a neutron flux of 10^{12}–10^{13} neutrons.cm^{-2}.sec^{-1} for 48 hr in the UAR-RR-1 Research Reactor at Inshass. After irradiation, samples were cooled for about 3 days. For an antimony standard, 0·2 ml of antimony(V) chloride solution (1·4 mg/ml) was evaporated to dryness in a quartz ampoule, and the ampoule was sealed off and irradiated along with the samples.

Processing of samples and standard. Each metal sample (about 300 mg) was freed from any surface contamination by brief washing in hydrochloric acid before being dissolved in concentrated hydrochloric acid to which had been added a few drops of concentrated nitric acid and 0·50 ml of antimony carrier solution. The sample solution was then evaporated nearly to dryness and then diluted to 25 ml with $6M$ hydrochloric acid containing potassium bromate ($5 \times 10^{-4}M$).

Each rock sample, after addition of 0·50 ml of antimony carrier solution, was dissolved in a platinum dish by heating repeatedly with a mixture of hydrofluoric, perchloric and nitric acids until silica was completely removed and a clear solution obtained. This solution was then evaporated nearly to dryness and diluted to 25 ml with the hydrochloric acid–potassium bromate solution.

The simultaneously irradiated antimony standard was dissolved in hot 6*M* hydrochloric acid containing a few drops of concentrated nitric acid and 0·05*M* potassium bromate solution. The standard solution was diluted to 25 ml with 6*M* hydrochloric acid. Subsequent dilutions were also made with 6*M* hydrochloric acid.

Losses of antimony in the course of dissolution of the samples and due to adsorption on glass were investigated as for ^{233}Pa.[8] Losses were found to be less than 1% in the presence of an antimony carrier.

Isopropyl ether extraction. Transfer 5 ml of the sample solution to a separatory-funnel and add to this solution 5 ml of isopropyl ether. Shake vigorously by hand for 4 min and separate the phases by centrifugation. Discard the aqueous layer. Transfer 5 ml of 1·5*M* hydrochloric acid to the funnel containing the organic phase and shake again for 4 min. Separate the phases and discard the aqueous layer. Measure the activity (*A*) of the organic layer with a single channel analyser.

Hexone extraction. Transfer 5 ml of the sample solution to a separatory-funnel and add to this solution 5 ml of hexone. Shake for 30 sec, and allow the phases to separate. Discard the aqueous fraction. Transfer 5 ml of 0·1*M* hydrochloric acid to the funnel and shake for 30 sec. Separate the phases and discard the aqueous layer. Measure the activity (*A*) of the organic layer.

TBP extraction. Transfer 5 ml of the sample solution to a separatory-funnel containing 2·5 ml of 12*M* lithium chloride solution. Add 5 ml of 50% TBP solution in xylene, this solution having been previously equilibrated with 10 ml of 6*M* hydrochloric acid. Shake for 30 sec. Allow the phases to separate and discard the aqueous layer. Add 15 ml of 1*M* nitric acid to the organic layer and shake the funnel for 30 sec. Discard the aqueous layer after phase separation. Measure the activity (*A*) of the organic layer.

Repeat the procedure used, on three 5-ml sample aliquots spiked with 50, 100 and 150 μl respectively of antimony standard solution. Measure the activity (A_m) of the final organic layer from each solution.

The antimony content (x) of a given sample is calculated from the relationship

$$x = \frac{x_s A}{A_m - A}$$

where x_s is the amount of standard added.[1]

RESULTS AND DISCUSSION

The results of determination of antimony in samples of aluminium, rock W-1 and piastre by the procedures described are presented in Table III.

TABLE III

Method	Sample	Weight of sample in aliquot, *g*	Activity,* *counts/30 sec/ml*	Sb content, *ppm*
Isopropyl ether extraction	Aluminium	0·1024	1588	0·058, 0·063, 0·054
	W-1	0·0148	3760	0·95, 1·2, 1·0(1·1†)
	Piastre‡	0·0520	61,650	4·65, 4·36, 5·10
Hexone extraction	W-1	0·0148	4824	1·05, 0·78, 0·96
	Piastre‡	0·0520	77,045	4·4, 4·5, 4·6
TBP extraction	Aluminium	0·1024	1573	0·055, 0·058, 0·056
	W-1	0·0148	4195	0·88, 0·95, 1·1
	Piastre‡	0·0520	67,843	4·73, 4·9, 4·4

* Activity of the ^{122}Sb + ^{124}Sb photopeaks at 0·564 and 0·603 MeV, respectively (channels 12–16).

† Average of the previously reported values.[10]

‡ Standard deviations 0·6, 0·2, 0·4 ppm for the isopropyl ether, hexone, and TBP methods respectively.

The radiochemical purity of the antimony extracts was demonstrated from the identity of the peaks of these extracts and of the simultaneously irradiated antimony standard (Fig. 1). Purity was also confirmed by the decay curves. From Fig. 1 it can be seen that the antimony separated is sufficiently pure for the analysis to be done with simple counters. The purity of the antimony separated from W-1 (a complex material containing varying proportions of almost all elements present in the periodic table) indicates the general applicability of the method. The given procedures are more simple and rapid than the methods reported in the literature for the neutron activation analysis of antimony.[11-18] Each of the procedures described here includes only two extraction steps, whereas the other published methods include 6 or 7 purification steps and the chemical yield of the isolated radioantimony must be determined. The hexone and TBP procedures are to be preferred to the isopropyl ether procedure because of their rapidity and the higher volatility of isopropyl ether.

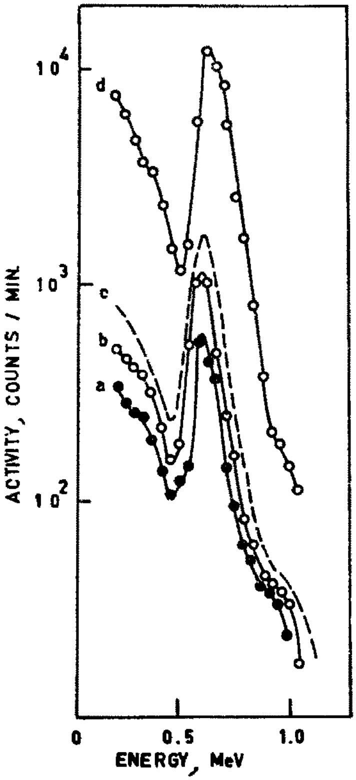

FIG. 1.—Gamma-ray spectra of Sb standard, and of extracts isolated from samples of W-1.
a—Isopropyl ether extract; *b*—TBP extract; *c*—Hexone extract; *d*—Irradiated Sb standard.

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Summary—The application of neutron activation analysis by standard addition and solvent extraction to the determination of traces of antimony in aluminium and rocks is reported. Three simple extraction procedures, using isopropyl ether, hexone, and tributyl phosphate, are described for the selective separation of radioantimony from interfering radionuclides. Antimony concentration is measured by counting the activities of the ^{122}Sb and ^{124}Sb photopeaks at 0·564 and 0·603 MeV.

Résumé—On décrit l'application de l'analyse par activation de neutrons avec addition d'étalon et extraction par solvant au dosage de traces d'antimoine dans l'aluminium et les roches. On décrit trois techniques d'extraction simples, utilisant l'éther isopropylique, l'hexone et le tributylphosphate, pour la séparation du radioantimoine des radionucléides gênants. On mesure la concentration de l'antimoine en comptant les activités des photopics de ^{122}Sb et ^{124}Sb à 0,564 et 0,603 MeV.

Zusammenfassung—Die neutronenaktivierungsanalytische Bestimmung von Antimonspuren in Aluminium und Gesteinen durch Zugabe eines Standards und Solventextraktion wird mitgeteilt. Es werden drei einfache Extraktionsvorschriften mit Isopropyläther, Hexon und Tributylphosphat zur selektiven Abtrennung von Radioantimon von störenden Radionukliden beschrieben. Die Antimonkonzentration mißt man durch Zählen der Aktivitäten in den Photopeaks von ^{122}Sb und ^{124}Sb bei 0,564 und 0,603 MeV.

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IN A RECENT communication, Sanke Gowda and Shakunthala[1] reported the use of chlorpromazine hydrochloride (CPH) as a new redox indicator in the vanadametric titration of iron(II) and molybdenum(V), and pointed out its advantages over diphenylamine, diphenylbenzidine, diphenylaminesulphonic acid, *N*-phenylanthranilic acid and copper–phthalocyaninetetrasulphonic acid, which have been proposed as internal indicators in vanadametry. A thorough study has now been made of the mechanism of the action and use of promethazine hydrochloride (PH), 10-(2-dimethylamino-1-propyl)phenothiazine hydrochloride, as a redox indicator in vanadametry.

The indicator gives a colourless aqueous solution, stable for about 2 weeks and then slowly undergoing atmospheric oxidation and becoming light pink. Like CPH it undergoes one-electron

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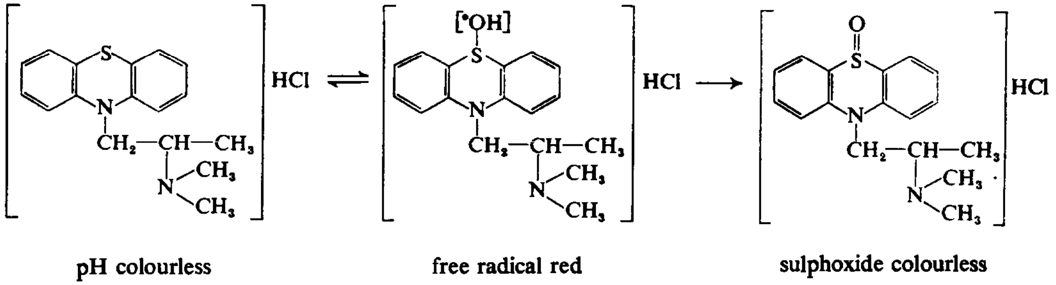
The indicator gives a colourless aqueous solution, stable for about 2 weeks and then slowly undergoing atmospheric oxidation and becoming light pink. Like CPH it undergoes one-electron oxidation to a red intermediate (believed to be a free radical with a semiquinonoid structure) which is further irreversibly oxidized (one electron) to a colourless sulphoxide:



Its behaviour is exactly similar to that of CPH.[3]

EXPERIMENTAL

Reagents

Promethazine hydrochloride. A 0·10% solution stored in an amber bottle.

Sodium vanadate solution. Approximately 0·05*N*, prepared from ammonium vanadate and sodium carbonate and standardized against standardized Mohr's salt solution.

Oxidation and transition potentials

The oxidation and transition potentials of PH were determined according to the procedures described previously.[1,3] The results are shown in Table I.

TABLE I.—OXIDATION AND TRANSITION POTENTIALS OF PH IN VARIOUS CONCENTRATIONS OF SULPHURIC ACID AT 28°C

Sulphuric acid, *M*	0·25	0·50	1·0	1·5	2·0
Oxidation potential, *V**	0·827	0·813	0·802	0·786	0·776
Transition potential, *V**	—	0·810	0·795	0·780	0·771

* Vs. standard hydrogen electrode.

Procedures

Determination of iron(II). Titrate iron(II) in 1*M* sulphuric acid or 1*M* hydrochloric acid containing 2–3 ml of syrupy phosphoric acid, using 1 ml of 0·1% PH solution.

Determination of hydroquinone. Titrate in 1*M* sulphuric acid or 1*M* hydrochloric acid, adding 2 ml of 0·5*M* oxalic acid as catalyst and 1 ml of 0·1% PH solution as indicator.

Determination of uranium(IV). Reduce uranium(VI) to uranium(IV) in a Jones reductor (in 1*M* sulphuric acid medium); pass a rapid stream of air through the reduced solution for about 10 min to oxidize any uranium(III) to uranium(IV). Add 20 ml of 2·5*M* sulphuric acid or 15 ml of 5*M* hydrochloric acid, 2 ml of syrupy phosphoric acid and 1 ml of 0·1% PH indicator solution, dilute to 50 ml and titrate with vanadate to the appearance of a violet colour.

Determination of antimony(III). Treat an aliquot of antimony trichloride solution with 100% excess of sodium vanadate in 4*M* sulphuric acid in a conical flask. Heat the solution on a boiling water-bath for about 2 min. Cool the solution to room temperature and dilute to give a 1*M* sulphuric acid solution. Titrate the surplus vanadate with standard 0·1*M* iron(II) ammonium sulphate, adding 1 ml of 0·1% PH solution near the end-point (after 90% titration).

RESULTS AND DISCUSSION

The maximum error found for titration of 0·1–0·6 mmole of hydroquinone, uranium(IV) and antimony(III) was 2 parts per 1000. Individual titrations are discussed below.

Iron(II)

The indicator colour change is from bluish green through blue to violet. End-points are not sharp if the acidity is <1*N* but can be detected with some practice in 1·2–1·8*N* acid media if the vanadate is added slowly towards the end-point (greenish blue → blue in sulphuric acid; bluish green → brownish yellow in hydrochloric acid). Sharp end-points (greenish blue through blue to violet in sulphuric aid; from green to brownish yellow in hydrochloric acid) are obtained in 2–4*N* acid media. At 2·8*N* acidity under-titration (1–2 drops of 0·05*N* vanadate) occurs owing to the low redox potential of the indicator but can be avoided by addition of phosphoric acid to change the equivalence potential. Phosphoric acid also prolongs the life and brightens the red colour of the oxidized form of the indicator.

At least 0·6 ml of 0·1% PH indicator solution is necessary in a total volume of 75 ml for proper indicator action. The red intermediate oxidation product of PH can be reversibly reduced to colourless PH by iron(II). The indicator correction found by comparing the results from the potentiometric titration with those when PH is used is 0·05 ml of 0·01*N* sodium vanadate for 1 ml of 0·1% PH.

PH is superior to CPH in that it functions over an acid range of 1·0–1·4*M* sulphuric acid or 1·0–2·0*M* hydrochloric acid even in the absence of phosphoric acid.

Hydroquinone

Diphenylbenzidine[4,5] and *N*-phenylanthranilic acid[5] are unsatisfactory because they give sluggish end-points. The redox potential of the hydroquinone–quinone system is 0·7 V while that of the vanadate–vanadyl system is 1·0 V, so the reaction between hydroquinone and vanadate in acid solution is likely to be fast. However, the titration of hydroquinone with vanadate has not been found feasible in sulphuric acid or hydrochloric acid media ranging from 0·5 to 5·0*N*. It has been found that the reaction between PH and vanadium(V) becomes slower with increasing concentration of quinone and vanadium(IV), the combined effect of quinone and vanadium(IV) being more than that of either individually. Oxalic acid has been found to act as an indicator catalyst. The end-point colour change for low hydroquinone concentrations (<1 mg/ml) is from parrot-green to violet, and is reversible. The violet colour is masked and seen as greenish pink in the titration of higher concentrations of hydroquinone. Oxalic acid brightens the violet colour but decreases its stability. The violet colour in 50 ml of titration mixture containing 2 ml of 0·5*M* oxalic acid is stable for about 4 min, and for 2 min if 6 ml are used. It is best to use low concentrations of hydroquinone and oxalic acid. PH indicator gives sharper end-points than do diphenylbenzidine and *N*-phenylanthranilic acid.

Uranium(IV)

N-phenylanthranilic acid[6,7] has been used in the titration of uranium(IV) with ammonium vanadate in 2·5–6·8*M* sulphuric acid. If oxalic acid is used as a catalyst the sulphuric acid concentration required is only 2*M*.[8] Diphenylbenzidine[8–10] has also been proposed as redox indicator with oxalate catalysis, titration being done at 50°; with both oxalic and phosphoric acids present it can be done at room temperature. Copper–phthalocyaninetetrasulphonic acid[11] functions only in 6*M* sulphuric acid solution containing 3 ml of syrupy phosphoric acid.

The formal redox potential of the uranium(VI)–uranium(IV) couple is 0·549 V in 0·5*M* sulphuric acid and increase with increasing concentration of sulphuric and phosphoric acids.[12] With smaller amounts of the indicator (0·1–0·6 ml of 0·1% PH solution) the colour change from bluish green through blue to violet is rather sluggish, but is sharp with larger amounts. PH indicator does not give sharp end-points in 0·2–2·0*M* sulphuric acid or hydrochloric acid unless phosphoric acid is present. Over this range of acidity under-titration occurs owing to the slow reduction of the oxidized form of the indicator by uranium(IV). Addition of a small amount of syrupy phosphoric acid (2 ml) catalyses this reduction, but sharp end-points are not obtained if the acidity is less than 1*N* even in the presence of phosphoric acid, owing to the high oxidation potential of the indicator. At higher acidities the reduction of the oxidized form of the indicator by uranium(IV) is again slow, resulting in the premature appearance of the end-point.

Antimony(III)

N-phenylanthranilic acid[13] and diphenylbenzidine[14] have been used as redox indicators in the vanadametric estimation of antimony(III). Antimony(III) cannot be titrated directly with sodium vanadate either in the cold or in the hot (80°) as the reaction is not rapid. Experiments on the oxidation of antimony(III) in the presence of a large excess of vanadate (75–150%) in varying concentrations of sulphuric acid (0·5–6*M*) at the temperature of the boiling water-bath for varying periods of time (1–15 min) show that antimony(III) is quantitatively oxidized if the sulphuric acid is 3–6*M* and the time taken is 2–15 min. The colour change from violet to greenish blue is quite sharp.

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Summary—Promethazine hydrochloride is proposed as a new redox indicator in vanadametry. It has been tested rigorously in the titration of iron(II), hydroquinone, uranium(IV) and antimony(III) with sodium vanadate. The indicator gives a very sharp reversible colour change from green to violet at the equivalence point. It has advantages over all the proposed redox indicators in vanadametry. Its redox and transition potentials are reported.

Zusammenfassung—Promethazin-Hydrochlorid wird als neuer Redox-Indikator bei der Vanadametrie vorgeschlagen. Es wurde bei der Titration von Eisen(II), Hydrochinon, Uran(IV) und Antimon(III) mit Natriumvanadat genau geprüft. Der Indikator gibt am Äquivalenzpunkt einen sehr scharfen reversiblen Farbumschlag von grün nach violett. Er hat Vorteile vor allen sonst bei der Vanadametrie empfohlenen Indikatoren. Seine Redox- und Übergangspotentiale werden mitgeteilt.

Résumé—On propose le chlorhydrate de prométhazine comme nouvel indicateur redox en vanadométrie. On l'a essayé de façon poussée dans les dosages du fer(II), de l'hydroquinone, de l'uranium(IV) et de l'antimoine(III) au moyen de vanadate de sodium. L'indicateur donne un changement de coloration très marqué et réversible du vert au violet au point d'équivalence. Il a des avantages sur tous les indicateurs redox proposés en vanadométrie. On donne ses potentiels redox et de transition.

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Precipitation of bis(1,2-cyclohexanedionedioximato)palladium(II) from homogeneous solution

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CYCLOHEXANEDIONEDIOXIME (nioxime) was first reported by Wallach in 1924.[1] Since that time several reports of its use as a gravimetric reagent for the determination of nickel have been published.[2-5] Only one account of nioxime as a reagent for palladium has appeared.[6] The reagent was found to be satisfactory for the analysis of samples containing 6–30 mg of palladium. However, filtration was difficult with the larger samples and separation from other ions was not better than with dimethylglyoxime. This and other methods for the gravimetric determination of palladium have been reviewed recently by Beamish.[7]

With a view to improving the gravimetric determination of palladium an attempt was made to precipitate bis(1,2-cyclohexanedionedioximato)palladium(II) from homogeneous solution by generating 1,2-cyclohexanedionedioxime in the presence of palladium ions. A method based on this

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With a view to improving the gravimetric determination of palladium an attempt was made to precipitate bis(1,2-cyclohexanedionedioximato)palladium(II) from homogeneous solution by generating 1,2-cyclohexanedionedioxime in the presence of palladium ions. A method based on this technique and applicable to samples containing 1–50 mg of palladium was developed. This paper contains a description of the method and a discussion of the results.

EXPERIMENTAL

Reagents

Palladium. Two grams of $PdCl_2$ (Fisher Scientific Company, Fair Lawn, New Jersey) were dissolved in 20 ml of 12*M* hydrochloric acid and diluted to 1 l., and the solution was standardized by precipitation with dimethylglyoxime.[8]

Hydroxylamine hydrochloride solution, 3% *w*/*v*.

1,2-*Cyclohexanedione.* The commercial product (Aldrich Chemical Company, Inc., Milwaukee, Wisconsin) was purified by sublimation and a solution containing 750 mg in 100 ml of distilled water was prepared and stored at 5°.

Platinum. Reagent grade chloroplatinic acid (1·3 g, Fisher Scientific Company, Fair Lawn, New Jersey) was dissolved in 500 ml of distilled water.

All other chemicals were reagent grade.

Procedure

To a solution containing 1–50 mg of palladium in a 400-ml beaker add 8 ml of 12*M* hydrochloric acid, 20 ml of hydroxylamine hydrochloride solution and 20 ml of 1,2-cyclohexanedione solution. Dilute to about 100 ml, stir, cover the beaker with a watch-glass and heat with a strong flame, bringing the solution to the boil in about 3 min. Reduce the flame and allow the mixture to boil for 5 min. Place the beaker in a cold water-bath for about ½hr. Filter off the precipitate, using a medium porosity sintered-glass crucible, wash it with cold water and dry it at 110° for 1 hr. Bis(1,2-cyclohexanedionedioximato)palladium(II) contains 27·37% of palladium.

RESULTS AND DISCUSSION

The effects of factors such as hydrochloric acid concentration, temperature of the reaction and concentration of the reagents on the amount, purity and physical characteristics of the precipitate were investigated. The best results were obtained when the precipitation was carried out in 0·3–1*M* hydrochloric acid. Good results were also achieved in the 0·1–0·3*M* range of acid concentration provided that the chloride ion concentration was at least 1*M*. The results of precipitations in the temperature range 20–90° were not very satisfactory. Accurate and reproducible results were always obtained when the solution was brought quickly to 100° and then boiled for 5 min.

Experiments showed that the minimum amounts of 1,2-cyclohexanedione and hydroxylamine hydrochloride required for a successful determination were 1·4 and 4·6 times their respective stoichiometric values. Very large excesses of these reagents (70 and 230 times the respective stoichiometric requirements) did not alter the results. Table I shows typical results that were found when the procedure was applied to various solutions.

Table I.—Separation and determination of palladium as Bis(1,2-cyclohexanedionedioximato)-palladium(II) by PFHS

Palladium taken, *mg*	1·08*	5·40*	16·18*	26·98*	53·95*	1·08	26·98	53·95
Diverse element taken, *mg*	none	none	none	none	none	Cu, 25 Ni, 25 Co, 25	Cu, 25 Ni, 25 Co, 25	Cu, 25 Ni, 25 Co, 25
Difference found, *mg*†	+0·01	+0·03	−0·02	+0·05	−0·05	+0·06	+0·05	−0·05
	+0·04	+0·01	−0·02	−0·03	−0·06	+0·01	+0·07	−0·10
	±0·00	−0·02	+0·05	−0·08	+0·03	+0·07	+0·06	+0·01
	+0·05		±0·00		+0·06			
	+0·06		+0·04		−0·03			

* Spectrophotometric[9] determinations showed that the palladium content in the filtrates never exceeded 0·02 mg.

† Difference found = mg of palladium found − mg of palladium taken.

Several experiments were done to observe the effect of various diverse ions on the determination. The results, shown in Table I, indicated that copper, nickel, and cobalt did not interfere. In order to avoid interference from platinum it was necessary to adjust the amount of 1,2-cyclohexanedione to the minimum (1·4 times the stoichiometric value) required for quantitative precipitation of the palladium. The exception was with samples containing 1–5 mg of palladium, in which case the amount of dione calculated for a 5-mg sample was used. Table II shows the results obtained after these adjustments were made to the recommended procedure.

TABLE II.—DETERMINATION OF PALLADIUM IN THE PRESENCE OF PLATINUM

Palladium taken, *mg*	1·08	16·18	26·98	53·95
Platinum taken, *mg*	25	25	25	25
Difference found, *mg*	+0·07 +0·03 +0·04	+0·06 +0·05 +0·11	+0·07 −0·09 −0·04	+0·04 −0·10 +0·06

The procedure described in this paper is simple, rapid and accurate. It is effective in the presence of large concentrations of Cu(II), Co(II), Ni(II), and Pt(IV) ions and yields a precipitate which is very easily filtered off and washed. In these respects it is better than other methods for the gravimetric determination of palladium.

Acknowledgement—We are grateful to the National Research Council of Canada for financial support.

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Summary—The reaction between hydroxylamine and cyclohexanedione in the presence of palladium ions has been made the basis of the precipitation of bis(1,2-cyclohexanedionedioximato)palladium(II) from homogeneous solution. The procedure provides a means of separating palladium from Cu(II), Co(II), Ni(II) and Pt(IV), and is a simple, rapid and accurate method for determining palladium.

Zusammenfassung—Die Reaktion von Hydroxylamin und Cyclohexandion in Gegenwart von Palladiumionen wurde zur Grundlage der Fällung von Bis(1,2-cyclohexandiondioximato)palladium(II) aus homogener Lösung gemacht. Die Vorschrift erlaubt die Abtrennung von Palladium von Cu(II), Co(II), Ni(II) und Pt(IV) und stellt eine einfache, schnelle und genaue Methode zur Palladiumbestimmung dar.

Résumé—On a pris la réaction entre l'hydroxylamine et la cyclohexanedione en présence d'ions palladium comme base pour la précipitation du bis(1,2-cyclohexanedionedioximato) palladium(II) à partir de solutions homogènes. La technique apporte un moyen de séparation du palladium des Cu(II), Co(II), Ni(II) et Pt(IV) et constitue une méthode simple, rapide et précise pour le dosage du palladium.

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Spectrophotometric determination of germanium(IV) with Bromopyrogallol Red

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THIS paper describes the use of dibromopyrogallolsulphonephthalein, $C_{19}H_{10}Br_2O_8S$, Bromopyrogallol Red (BPR), as a reagent for the spectrophotometric determination of germanium(IV).

EXPERIMENTAL

Figure 1 shows the absorption spectra of BPR (curve a) and of the Ge(IV)–BPR compound (curve b), and shows that the absorption maximum of the Ge(IV)–BPR compound is at 550 mμ whereas that of the reagent is at 436 mμ.

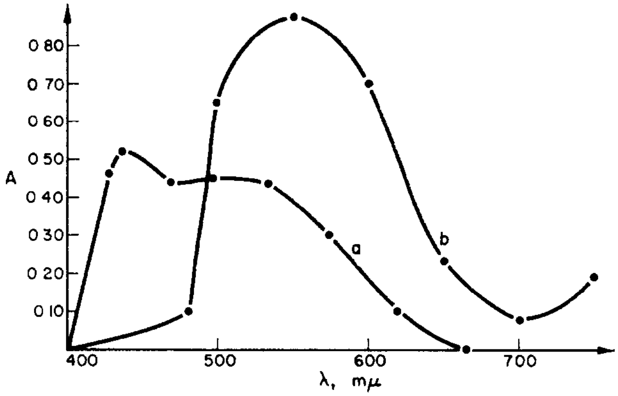

FIG. 1.—Absorption spectra.
(*a*)—BPR, 3 × $10^{-5}M$; (*b*)—$Ge(BPR)_2$ complex.

The absorbance of the complex was studied as a function of pH. It was found that glycine–hydrochloric acid or phthalate–hydrochloric acid solutions may be used as buffers for the pH range 2–3. The absorbance of the complex was also measured as a function of hydrochloric acid concentration; maximum absorbance was found between 10^{-2} and $10^{-3}M$.

The hydrochloric solutions of the complex, stabilized with 0·5% gelatine solution, are very stable, in spite of their colloidal character. Maximum absorbance is attained within 15 min and remains constant for several days.

Reagents

Germanium(IV) solution. High-purity germanium dioxide was dissolved to give a standard solution containing 6 ppm germanium(IV).

Bromopyrogallol Red solution 0·025%. Prepared in 50% aqueous ethanol.

Gelatine solution, 0·5%. Prepared immediately before use.

Procedure

Standard curve. Place aliquots of the standard germanium solution in 50-ml volumetric flasks and add 2·5 ml of 0·1*M* hydrochloric acid (to give a final solution with pH 2–3), 5 ml of 0·5% gelatine solution and 15 ml of BPR solution. Make up to the mark with distilled water. Shake the mixture and then keep it for 15 min at room temperature. Measure the absorbance in 1-cm cuvettes against a blank at 550 mμ. Use a similar procedure for samples.

RESULTS AND DISCUSSION

The Lambert–Beer law is obeyed over the range 0·2–3 μg of Ge per ml. The molar absorptivity is 20·5 × 10^3.

Job's method was used to determine the stoichiometry of the complex (Fig. 2); the stoichiometric ratio is Ge:BPR = 1:2.

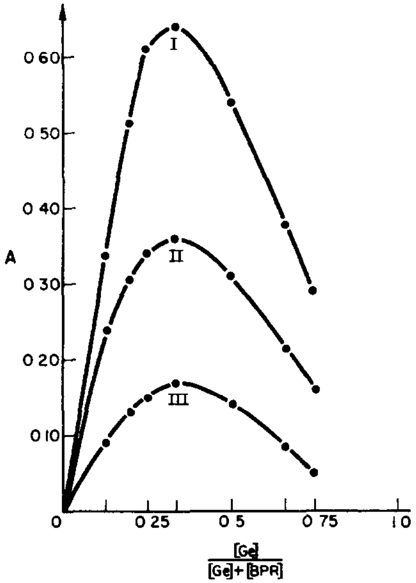

FIG. 2.—Method of continuous variations with equimolar solutions.
I—1·5 × $10^{-4}M$; II—$10^{-4}M$; III—5 × $10^{-5}M$.

The complex has a red-violet colour and is insoluble in common organic solvents, carbon tetrachloride, chloroform, ethyl ether, amyl alcohol, benzene, methyl ethyl ketone, methyl isobutyl ketone, *etc.*

BPR has been used to determine germanium in several cupriferous materials, following dissolution by nitric, phosphoric and hydrofluoric acids and subsequent extraction with carbon tetrachloride from 9–10*M* hydrochloric acid.[1] It was found that recovery was essentially complete, and that a calibration curve prepared by treating germanium back-extracted from the organic phase according to the standard procedure was almost identical with the standard curve prepared as directed above.

The cupriferous materials analysed had the approximate composition: Cu, 5·5%; S, 41·5%; Fe, 40–50%; Zn, 2–3%; Pb, 1%; As, 0·3%; SiO_2, 1·5%; In, 0·005%; Te, 0·1%; Au, 0·002%; Se, 0·01%; Ag, 0·02%; and Ga, 0·2%. The germanium was determined spectrophotometrically by the phenylfluorone method[3] and the method described here. Results are shown in Table I.

TABLE I.—DETERMINATION OF GERMANIUM IN CUPRIFEROUS ORE

Ore sample, *g*	Ge found, %	
	Phenylfluorone	BPR
1·3594	0·022	0·023
1·7418	0·024	0·021
1·1433	0·024	0·022
1·2872	0·021	0·020

This procedure, in terms of sensitivity, selectivity and stability of coloured complex, is more advantageous than those based on gallein[5] and Pyrocatechol Violet.[4]

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Summary—A method is proposed for the spectrophotometric determination of germanium with Bromopyrogallol Red. A red-violet coloured complex is formed at pH 2–3, with a stoichiometry equivalent to $Ge(BPR)_2$, and a molar absorptivity of $20{\cdot}5 \times 10^3$ at 550 mμ. Beer's law is obeyed over the range 0·2–3 ppm. Germanium in cupriferous ores has been determined by the method.

Résumé—On propose une méthode pour le dosage spectrophotométrique du germanium au Rouge de Bromopyrogallol. A pH 2-3 il se forme un complexe coloré en rouge-violet, avec une stoechiométrie équivalent à $Ge(BPR)_2$ et une absorption moléculaire de $20{,}5 \times 10^3$ à 550 mμ. La loi de Beer est suivie dans le domaine 0,2 à 3 p.p.m. On a déterminé le germanium par cette méthode dans des minerais cupriferreux.

Zusammenfassung—Ein Verfahren zur specktrophotometrischen Bestimmung von Germanium mit Brompyrogallolrot wird vorgeschlagen. Bei pH 2–3 wird ein rotvioletter Komplex mit der Stöchiometrie $Ge(BPR)_2$ und einem molaren Extinktionskoeffizienten von $20{,}5 \times 10^3$ gebildet. Das Beersche Gesetz gilt bei 0,2–3 ppm. Mit dieser Methode wurde Germanium in Kupfererzen bestimmt.

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Polarography of molybdenum in aspartic acid solution

(*Received* 2 *February* 1967. *Revised* 1 *June* 1967. *Accepted* 20 *August* 1967)

A NUMBER of polarographic methods, many requiring preliminary separations, have been described for the determination of molybdenum.[1–5] Meites,[6] Přibil,[7] and Parry[8] have given methods for its determination in the presence of tungsten, using as electrolytes solutions containing citrate, EDTA, and tartrate respectively. Deshmukh determined molybdenum in the presence of uranium, using a solution of hydrazine sulphate as electrolyte.[9] Manning used nitrilotriacetic acid as electrolyte[10] and found four reduction waves, enabling determinations to be made in the presence of Cu, Ti, Ni, Cr, Hg, and Th. More recently Hahn studied the variation in the polarographic characteristics with pH in citrate-containing media.[11] Pantani reported that molybdenum(VI) is also reduced in solutions of oxalate, tartrate, and citrate.[12] This paper reports the results of an investigation into the use of aspartic acid as a suitable electrolyte for the polarographic determination of molybdenum, following similar investigations into the use of other electrolytes.[13–14] Interferences from a number of metals have been studied.

EXPERIMENTAL

All chemicals used were of reagent grade, and the solutions were prepared in doubly distilled water. The pH of solutions was adjusted by addition of $1M$ hydrochloric acid to sodium aspartate solutions.

A manual polarograph with a "Scalamp" galvanometer was used. The dropping mercury electrode had the following characteristics: $m = 2{\cdot}24$ mg/sec, $t = 3{\cdot}04$ sec. Purified hydrogen was bubbled through the sample solutions to remove dissolved oxygen. An H-type cell was used with a saturated calomel electrode and an agar-saturated potassium chloride salt bridge. All measurements were made at 25°C.

DISCUSSION

Molybdenum(VI) is reduced at the dropping mercury electrode (DME) in $0{\cdot}1M$ sodium aspartate at pH 4, and for a concentration of $10^{-3}M$ the $E_{\frac{1}{2}}$ is $-0{\cdot}62$ V. The hydrogen wave occurs at $-1{\cdot}2$ V

Summary—A method is proposed for the spectrophotometric determination of germanium with Bromopyrogallol Red. A red–violet coloured complex is formed at pH 2–3, with a stoichiometry equivalent to $Ge(BPR)_2$, and a molar absorptivity of $20·5 \times 10^3$ at 550 mμ. Beer's law is obeyed over the range 0·2–3 ppm. Germanium in cupriferous ores has been determined by the method.

Résumé—On propose une méthode pour le dosage spectrophotométrique du germanium au Rouge de Bromopyrogallol. A pH 2-3 il se forme un complexe coloré en rouge-violet, avec une stoechiométrie équivalent à $Ge(BPR)_2$ et une absorption moléculaire de $20,5 \times 10^3$ à 550 mμ. La loi de Beer est suivie dans le domaine 0,2 à 3 p.p.m. On a déterminé le germanium par cette méthode dans des minerais cupriferreux.

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DISCUSSION

Molybdenum(VI) is reduced at the dropping mercury electrode (DME) in $0·1M$ sodium aspartate at pH 4, and for a concentration of $10^{-3}M$ the $E_{1/2}$ is $-0·62$ V. The hydrogen wave occurs at $-1·2$ V in this medium. The diffusion current decreases with increasing negative potential after a maximum. At lower pH (in 0·01 M aspartic acid solution) two waves are found, the height of the first being about half the height of the second, suggesting that reduction occurs first to Mo(V) and then to Mo(III). Figure 1 shows such a polarogram.

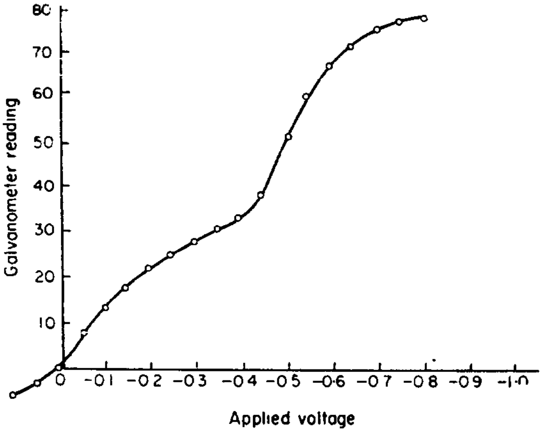

FIG. 1.—Polarogram of $2 \times 10^{-4}M$ molybdenum(VI) in $0{\cdot}01M$ aspartic acid.

The total diffusion current, corrected for the residual current, has been found to be proportional to the concentration of molybdenum(VI) over the range 10^{-3}–$10^{-5}M$, when measured at pH 4 and $-1{\cdot}0$ V *vs.* the SCE. At higher concentrations, the wave is shifted in a negative direction along the potential axis.

The diffusion coefficient for the reducible species, assuming a three-electron transfer, is calculated to be $1{\cdot}44 \times 10^{-5}$ cm^2 sec^{-1}, about 30% higher than that for chromate ions ($1{\cdot}1 \times 10^{-5}$). This may be due to the existence of a polymerized species, which may be an aspartate complex. The degree of polymerization does not appear to change with the total molybdenum concentration, as the diffusion coefficient remains constant.

The plots of $\log i/(i_d - i)$ *vs.* E gave a slope of 0·11, from which it was concluded that the electrode reactions were irreversible. The total diffusion current was found to be proportional to the square root of the height of the mercury column, showing that the reduction wave is diffusion controlled. The diffusion current increases by 2·4%/deg over the temperature range 25–45°.

The decrease in the diffusion current with increasing negative potential may be explained by assuming that adsorption of the reducible species is necessary before reduction can occur, so that the current becomes less because not all of the ions reaching the electrode are adsorbed and reduced.

The half-wave potentials of the molybdenum(VI) waves are shifted to more negative values at higher pH, as shown in Fig. 2.

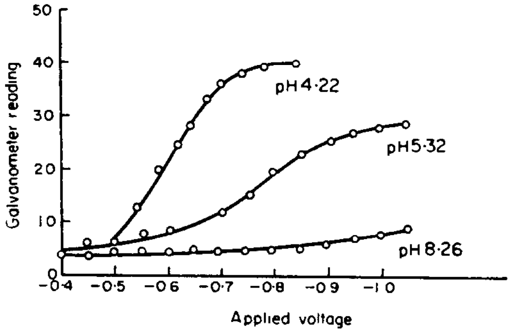

FIG. 2.—Polarograms of $10^{-3}M$ molybdenum(VI) in $0{\cdot}1M$ sodium aspartate at various pH values.

Interfering ions

Tungsten is not reduced at the dropping mercury electrode in $0{\cdot}1M$ aspartic acid, but when present in greater than 100-fold molar excess over the molybdenum, it does interfere. It is possible that tungsten forms a complex with aspartic acid that is stronger than the molybdenum one. The optimum concentration for the determination of molybdenum in the presence of large excesses of tungsten is around $6 \times 10^{-4}M$. The method of standard additions is recommended, and the error is about 1%.

Molybdenum may also be determined in the presence of Co(II), Ni, Cu(II), Mn(II), Th, or Cr(VI). Cobalt is not reduced at the DME, but nickel is, ($E_{\frac{1}{2}} = -1{\cdot}08$ V) in the aspartic acid solution. When the concentration of either is less than the concentration of the molybdenum the interference is negligible. Chromate gives an anodic wave, but small amounts (1/20 that of the molybdenum) can be tolerated. Copper is reduced with $E_{\frac{1}{2}} = -0{\cdot}08$ V, and small amounts (1/50 that of the molybdate) can be tolerated. Gelatin should be added when chromate or copper is present. Manganese is not reduced, and does not interfere, while thorium is reduced at a more negative potential and quantities equal to the amount of molybdenum can be tolerated.

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Summary—The polarographic behaviour of Mo(VI) in solutions of aspartic acid is reported. In $0{\cdot}01M$ acid, two waves are obtained, but at pH 4 only one, and they are diffusion controlled. The determination is possible in the presence of Ni, Cr(VI), W(VI), Mn(II), Co(II), Cu(II) or Th, with an accuracy of 2% in the range 10^{-5}–$10^{-3}M$.

Zusammenfassung—Es wird über polarographische Verhalten von Mo(VI) in Asparaginsäure enthaltenden Lösungen berichtet. In $0{,}01M$ Säure werden zwei Stufen erhalten, bei pH 4 jedoch nur eine; sie sind diffusionskontrolliert. Die Bestimmung ist in Gegenwart von Ni, Cr(VI), W(VI), Mn(II), Co(II), Cu(II) oder Th mit einer Genauigkeit von 2% im Bereich 10^{-5}–$10^{-3}M$ möglich.

Résumé—On décrit le comportement polarographique du Mo(VI) en solutions d'acide aspartique. En acide $0{,}01M$ on obtient deux vagues, mais à pH 4 une seulement, et elles sont contrôlées par diffusion. Le dosage est possible en présence de Ni, Cr(VI), W(VI), Mn(II), Co(II), Cu(II) ou Th, avec une précision de 2% dans le domaine 10^{-5}–$10^{-3}M$.

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LETTER TO THE EDITOR

Exchange reactions on columns

SIR,

Successful determinations based on exchange reactions on columns have been reported from time to time in the literature; for example, Lambert and Yasuda[1] have reported satisfactory results in determining chloride ions with a column of granular silver iodate. Such methods do not appear to have come into general use, for it has not been possible to find any account of further critical studies of the recommended procedures. Because there is a considerable need in the field of analysis of acid radicals for a method of determining concentrations of sulphate and chloride ions at the 1 μg/ml level, several exchange reactions have been studied[2] from the aspect of their behaviour on columns. Such a combination would be attractive in that, with a colorimetric end-determination, it could be adapted to automatic methods of analysis.

Barium sulphate is the most insoluble of the commonly-known sulphates and was used in exchange reactions by causing the sulphate ions to react with a rather less insoluble barium salt deposited on a column of pumice-stone. Three barium salts were investigated—chromate, molybdate and chloranilate.[3] Barium chromate columns gave reasonably low blanks when 50% v/v ethanol–water mixtures were used as solvent. However, only 5–15% of the sulphate ions reacted when passed down the columns, presumably because there was an insufficient solubility difference between barium chromate and barium sulphate to drive the exchange reaction to completion. Barium molybdate is more soluble than the chromate and so a substantial reaction occurred but the blanks were correspondingly higher. Barium chloranilate was not sensitive enough at the 1 μg/ml level of sulphate to give a colour intensity distinguishable from that of the blanks.

Mercury(I) and mercury(II) iodates and periodates were used on pumice-stone for determining low concentrations of chloride ions. The possibility of chloride ions reacting with these materials depended on the greater insolubility of mercury(I) chloride or on the low degree of dissociation of mercury(II) chloride. The iodate and periodate ions released were determined by the amplification reaction with potassium iodide. Mercury(I) iodate gave reasonably low blanks but only 50% and 94% reaction at the 1 and 50 μg/ml levels of chloride ions respectively. Mercury(II) periodate also gave satisfactory blanks but incomplete reaction. The remaining two mercury compounds gave high blanks in addition to incomplete reactions. In all four cases the incomplete reactions were most probably due to the relative solubilities or degrees of dissociation of the reactants and products being insufficiently different for completion of the reactions.

The results obtained with the seven columns investigated showed that, for 1 μg/ml concentrations, the blanks were too high and/or reaction was incomplete. It appears that it is virtually impossible to find a material that will give a perfect compromise because a material insoluble enough to give a low blank would provide insufficient difference from the product solubility for the reactions to go to completion.

In their work Lambert and Yasuda[1] made use of the factor of 30 in the respective solubilities of silver iodate and silver chloride. There is only a factor of 4·5 between the solubilities of barium chromate and barium sulphate. However, the lowest concentration of chloride ion used was 30 ppm (*i.e.*, 30 μg/ml) at which concentration the blanks amounted to only 5% of the chloride measured. Barium molybdate is 26 times as soluble as barium sulphate and this favours reaction, but the high blanks obtained would restrict the method to higher sulphate concentrations, for which other existing methods would probably be used.

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20 *September* 1967

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RAPID DETERMINATION OF COPPER IN PLANTS BY NEUTRON ACTIVATION ANALYSIS

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Summary—A rapid and simple neutron-activation analysis method has been developed for the determination of copper in plant leaves. Irradiated samples are dissolved in a mixture of fuming nitric acid, 70% perchloric acid and concentrated sulphuric acid in the presence of copper carrier solution. The copper in the resulting solution is extracted as copper cupferronate into chloroform and back-extracted into concentrated ammonia solution. The copper is precipitated as sulphide with 3% aqueous thioacetamide solution and the precipitate is dissolved in nitric acid. The induced activity of copper-64 in the resulting solution is counted with a 400-channel analyser. The photopeak of the annihilation energy of copper-64 at 0·51 MeV is compared with that of a copper standard processed in the same manner. After counting, the chemical yield of the separated copper is found by re-irradiating aliquots of the copper nitrate solution and comparing the induced activity of copper-66 at 1·04 MeV with that of another standard processed in a similar manner. The time required to complete the analysis, including the second irradiation and all radioactivity measurements, is about 25 min. The accuracy of the method was checked by analysing a biological standard of known copper content. The proposed method was successfully applied to the determination of copper in the leaves of 10 different plants (copper content 4–30 ppm).

COPPER has been long known as an essential trace element for the growth of plants.[1] Neutron-activation analysis, with its advantages of high sensitivity and elimination of reagent blanks, is considered one of the best methods for the estimation of copper in any biological tissue. The determination of copper in different materials by this method has been reported.[2–7]

Non-destructive activation analysis in conjunction with gamma scintillation spectroscopy cannot be successfully applied for determining copper in plant tissues, mainly because the isotopes of manganese, sodium and potassium also present after irradiation seriously interfere with the measurement of the induced activity of copper-64 or copper-66.

Several workers have used radiochemical separations based on precipitation,[8–10] ion-exchange,[11–13] paper chromatography[14] or electrodeposition methods,[15,16] combined with activation analysis to determine copper in plants. Such methods give an excellent degree of radiochemical purity for copper but are time-consuming and are practicable only if they are used in conjunction with the determination of other trace elements. On the other hand, solvent extraction methods[17] are suitable for fast radiochemical separations of many elements including copper.

Kaiser and Meinke[18] developed a very rapid activation analysis method for determining copper in biological tissue by applying extraction and precipitation methods to isolate copper, and measuring the induced activity of copper-66. However, the chemical yield correction for copper was made iodometrically after counting.

The simple and rapid technique of re-activation for determining the chemical yield of a short-lived radionuclide and its carrier after a radiochemical separation was first applied by Kamemoto and Yamagishi[19–21] for aluminium, vanadium and magnesium. The same technique has been applied in the present work for the chemical yield correction of copper.

This paper describes a simple, rapid and accurate activation analysis method for the determination of copper in the leaves of different plants. The method is a combination of destructive and non-destructive activation analysis in which copper-64 after a fast radiochemical separation, and copper-66 after re-activation, are counted.

The fast-neutron induced reaction ^{64}Zn(n, p)^{64}Cu is unlikely to interfere with the determination of copper in plants. The amount of zinc in plants[23] is usually less than 100 μg/g, from which amount the ^{64}Cu produced by the reaction above is equivalent to only 0·07 μg of copper,[24,25] which is about 1/100 of the normal copper content in plants.

TABLE I.—NUCLEAR DATA FOR THERMAL NEUTRON ACTIVATION OF COPPER[22]

Stable isotopes	Natural abundance %	Activation cross-section, *barns*	Product of thermal neutron irradiation	Half-life	Mode of decay	Energy of radiation, *MeV*
^{63}Cu	69·1	4·3	^{64}Cu	12·8 hr	β, γ	0·57β⁻, 0·65β⁺, 1·34γ (weak)
^{65}Cu	30·9	1·8	^{66}Cu	5·1 min	β, γ	2·65β⁻, 1·04γ, others (weak)

EXPERIMENTAL

Apparatus

Pulse height analyser. An NaI(Tl) crystal (3 × 3 in.) coupled with an Intertechnique 400-channel gamma spectrometer SA-40.

Scintillation counter. An NaI(Tl) well-type scintillation crystal (2 × 1·75 in.) connected with a single-channel analyser.

Reagents

Analytical reagent grade materials were used.

Copper carrier solution. Dissolve "spectrographically-pure" copper metal foil in 1% nitric acid to provide a solution containing 10 mg of copper per ml.

Copper standard solutions. Standardize the copper carrier solution and dilute it to give solutions containing (*A*) 50 μg of copper per ml, and (*B*) 2 mg of copper per ml.

Copper radiotracer. Irradiate 50 mg of "spectrographically-pure" grade copper metal foil at a neutron flux of about 2×10^{12} n cm^{-2} sec^{-1}. Allow the irradiated sample to cool for 2 hr so that the induced activity of ^{66}Cu will decay to a negligible amount. Dissolve the copper foil in 2 ml of concentrated nitric acid and make up to 50 ml with water in a standard flask.

Sodium chloride hold-back carrier solution. Prepare an aqueous solution of sodium chloride containing 10 mg of sodium per ml.

Manganese sulphate hold-back carrier solution. Prepare an aqueous solution of manganese sulphate containing 20 mg of manganese per ml.

Preparation of samples for irradiation

The plant leaves were washed with detergent, rinsed with distilled water and oven dried at 75° to constant weight. The dried samples were ground with a perspex mill.

Irradiation

All neutron irradiations were carried out in the "Democritos" Reactor of the Nuclear Research Centre of Greece, using the pneumatic transfer (rabbit) system.

The samples weighing 150–200 mg each, were placed in polyethylene tubes (10 × 30 mm). Aliquots of 0·5 ml of the standard copper solution *A* were transferred by pipette into identical polyethylene tubes. The tubes were heat-sealed, wrapped in plastic sheets and irradiated for 35 min in a thermal flux of about $2{\cdot}2 \times 10^{12}$ n cm^{-2} sec^{-1}

A second irradiation at the same flux was performed to determine the chemical yield correction for copper isolated by the proposed radiochemical procedure Details are given under *Chemical yield determination.*

DEVELOPMENT OF METHOD

Extraction experiments

Several experiments were carried out in order to establish the radiochemical separation of copper by extraction as copper cupferronate into chloroform from different concentrations of nitric, perchloric and sulphuric acids, the acids used for the dissolution of plants. Copper carrier and copper radiotracer solutions were used. After the extraction of copper into chloroform and the equilibration of the two phases, aliquots of each phase were withdrawn for γ-radioactivity measurements with the scintillation counter. The time of extraction was 1·5 min; the phase ratio, organic to aqueous, was 1:2. The concentrations of copper and cupferron were $3{\cdot}2 \times 10^{-3}M$ and $0{\cdot}13M$ respectively. As can be seen from Fig 1, in the absence of acids the extraction of copper into chloroform is about 99% complete, but with an increase of sulphuric acid concentration there is a continuous drop in the extraction of copper. The same is true for perchloric and nitric acids but the drop is sharper. However, at low concentrations of acid, *e.g.*, at 0·5*N*, the extraction of copper is greater than 88% for all acids. Thus, by simple dilution of the solution resulting from the wet-oxidation of plants, the proper condition for copper extraction are obtained without any further chemical step.

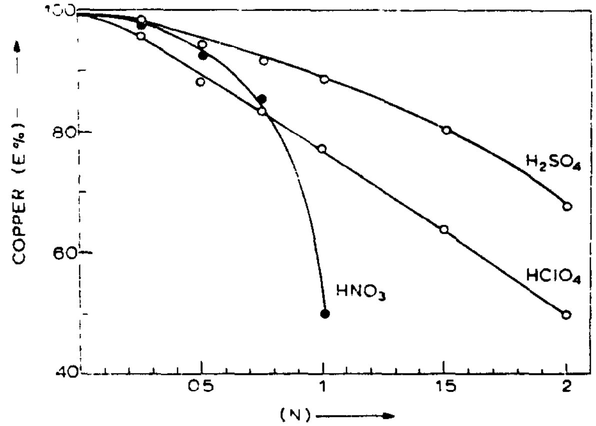

FIG. 1.—Effect of H_2SO_4, $HClO_4$ and HNO_3 concentration on the extractability of copper cupferronate with chloroform.

Back-extraction experiments have shown that copper extracted into chloroform can be stripped from the organic phase with better than 96% efficiency by thoroughly shaking it for 1 min with 15 ml of concentrated ammonia solution.

Re-irradiation

One-ml aliquots of the copper standard solution *B* were transferred into polyethylene tubes and irradiated for a time ranging from 5–100 sec. It has been found that an irradiation time of 45 sec is a proper time for good counting statistics when counting is for a 30-sec period. In order to minimize errors due to geometry, molten paraffin was cast into a 10-ml Erlenmayer flask containing a polyethylene tube to produce a hole in which the irradiated polyethylene tubes could be inserted for counting.

Procedure

After the irradiation, open the samples and standards behind a shield. Transfer each sample into a 100-ml beaker containing 1 ml of copper carrier solution and 1 ml of each of the hold-back carrier solutions of manganese and sodium. Add 3 ml of fuming nitric acid, 2 ml of 70% perchloric acid and 1 ml of concentrated sulphuric acid, and heat the beaker over a bunsen burner until white fumes of perchloric acid are evolved. Cool, add 35 ml of water, and after dissolution, cool the beaker in an ice-bath to room temperature. Decant the solution into a 100-ml separatory-funnel containing 25 ml of chloroform and 15 ml of 6% aqueous cupferron solution. Shake the contents for 1·5 min and leave the two phases to equilibrate for 0·5 min. Transfer the organic phase to a second separatory-funnel containing 15 ml of concentrated ammonia solution. To the first separatory-funnel add 25 ml of chloroform and shake the contents for 1 min. After equilibration transfer the organic phase to the separatory-funnel containing the ammonia and the chloroform layer from the first extraction. Shake the contents for 1 min and after equilibration discard the organic phase and draw off the aqueous phase into a 50-ml centrifuge tube containing 10 ml of 3% aqueous thioacetamide solution. Centrifuge the mixture, discard completely the supernatant liquid, wash the copper sulphide precipitate with 10 ml of distilled water and centrifuge again. After centrifugation, decant the supernatant liquid and dissolve the precipitate in 2 ml of concentrated nitric acid by heating the centrifuge tube over a burner. Transfer the resulting solution of copper nitrate into a 5-ml volumetric flask. Wash the centrifuge tube with 2 ml of distilled water with the aid of a washing-bottle and decant the washings into the same flask. Dilute to volume with water, mix, and count the contents of the flask. Transfer with a micropipette 100 μl of the irradiated copper standard solution *A* into a 100-ml beaker containing 1 ml of copper carrier solution and 1 ml of each of the hold-back carrier solutions of sodium and manganese. Follow the same procedure used for the plant sample.

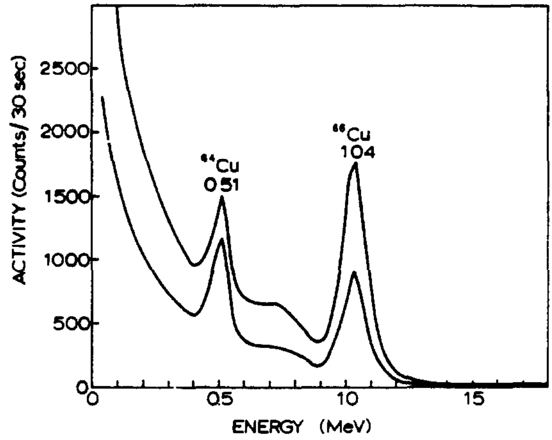

FIG. 2.—Gamma-ray spectra of copper-64 and copper-66 after re-activation, taken at 5-min intervals.

Activity measurements

Take a 4-min count of the volumetric flasks containing the copper solutions isolated from the irradiated samples and the standards, on the crystal of the multichannel analyser. Compare the areas under the ^{64}Cu 0·51-MeV annihilation energy photopeak for the samples and standards according to the method reported by Covell.[26] A γ-ray spectrum of an irradiated sample was taken after the radiochemical separation of copper and shown to be that of pure ^{64}Cu. Gamma-ray contaminants were not apparently present. This was also checked by making decay studies and determining the half-life of ^{64}Cu. The value found corresponds to the one reported in the literature.[27] It has been also found by radiotracer experiments that decontamination factors of 7×10^5 for manganese and $>10^6$ for arsenic, potassium, sodium and zinc are obtained by the proposed radiochemical procedure.

Determination of chemical yield

Immediately after counting, the chemical yield of the isolated copper was determined by re-activation. Since it is the ^{66}Cu induced activity which is measured after re-activation it is not necessary to wait for the decay of ^{64}Cu counted after the first irradiation. Aliquots of 1 ml of the copper nitrate solution in the volumetric flasks, were transferred by pipette into polyethylene tubes, and 1-ml aliquots of copper standard solution *B* into identical polyethylene tubes. The tubes were heat-sealed, wrapped in plastic sheets and irradiated for 45 sec at a thermal flux of about $2{\cdot}2 \times 10^{12}$ n cm^{-2} sec^{-1}. The irradiated tubes were placed in the paraffin block in the small Erlenmayer flask (see *Re-irradiation*) and counted on the crystal of the multi-channel analyser for 30 sec. The areas under the 1·04-MeV ^{66}Cu photopeak were evaluated according to the method of Covell.[26] The relative standard deviation of the re-activation procedure is ±2·8%. The chemical yield of copper averaged 78%.

The pure γ-ray spectra of ^{64}Cu and ^{66}Cu taken after re-activation at 5-min intervals are shown in Fig. 2.

RESULTS

Results of the determination of copper in the leaves of 10 different plants are listed in Table II. The results given are the mean values of at least triplicate analyses. The accuracy and reproducibility of the method were checked with the aid of a biological standard, 10 samples of which were analysed by the proposed method. The amount of copper found in the biological standard was 4·4 μg per gram of dried matter. This value is in very good agreement with the copper content found by other laboratories for the same sample.[28] The overall relative standard deviation was ±5·5%. The time required to complete the analysis after the first irradiation is about 25 min, including the second irradiation and all radioactivity measurements. This time is made up as follows.

TABLE II.—DETERMINATION OF COPPER IN THE LEAVES OF PLANTS

Plant	Copper, μg/g	Plant	Copper, μg/g
Olive tree	5·0	Cotton	10·7
Orange tree	4·3	Sugar beets	13·7
Pine tree	5·3	Tobacco	30·8
Tangerine tree	6·1	Alfalfa	9·6
Corn	5·9	Grass	9·0

Results are means of 3 analyses and are referred to dried samples.

Dissolution of sample		4 min
Double extraction of copper		4 min
Back-extraction—precipitation of copper		2 min
Centrifugation—washing of precipitate		4 min
Dissolution of precipitate and preparation for counting		3 min
Counting		4 min
Re-irradiation procedure:		
Preparation of sample for re-irradiation	1·50 min	
Re-irradiation time	0·75 min	
Elapsed time before counting	1·25 min	
Counting	0·50 min	4 min
		25 min

A minimum of 0·3 μg of copper can be determined by this method, with a 35 min irradation, but this minimum could be lowered by at least 2 orders of magnitude if the duration of irradiation was increased to 12 hr.

CONCLUSION

The method is characterized by its rapidity, simplicity, and accuracy making it convenient for a series of analyses. The induced activity of ^{64}Cu in the first irradiation and ^{66}Cu in the second irradiation are used for the determination and the chemical yield of copper respectively. It is considered that the same neutron-activation technique can also be applied to the determination of copper in any biological material.

Acknowledgements—The author is indebted to Dr. H. J. M. Bowen who supplied the biological standard sample. He wishes also to thank Dr. N. Yassoglou and Dr. T. Hayes for helpful discussions, as well as Miss Mary Phoka for valuable assistance in developing this method and Mrs. A. Saropoulou for performing part of the radioactivity measurements.

Résumé—On a élaboré une méthode rapide et simple d'analyse par activation de neutrons pour le dosage du cuivre dans des feuilles de plantes. Les échantillons irradiés sont dissous dans un mélange d'acide nitrique fumant, d'acide perchlorique 70% et d'acide sulfurique concentré en présence d'une solution d'entraineur de cuivre. Le cuivre de la solution résultante est extrait à l'état de cupferronate de cuivre en chloroforme et réextrait dans une solution concentrée d'ammoniaque. On précipite le cuivre à l'état de sulfure par une solution aqueuse à 3% de thioacétamide et dissout le précipité dans l'acide nitrique. L'activité induite du cuivre-64 dans la solution résultante est comptée avec un analyseur 400 canaux. On compare le photopic de l'énergie d'annihilation du cuivre-64 à 0,51 MeV à celui d'un étalon de cuivre traité de même manière. Après comptage, on trouve le rendement chimique du cuivre séparé en irradiant de nouveau des parties aliquotes de la solution de nitrate de cuivre et en comparant l'activité induite du cuivre-66 à 1,04 MeV à celle d'un autre étalon traité de manière semblable. Le temps nécessité pour effectuer l'analyse, y compris la seconde irradiation et toutes les mesures de radioactivité, est d'environ 25 mn. On a contrôlé la précision de la méthode en analysant un étalon biologique à teneur en cuivre connue. La méthode proposée a été appliquée avec succès au dosage du cuivre dans les feuilles de 10 plantes différentes (teneur en cuivre 4–30 p.p.m.).

Zusammenfassung—Eine schnelle und einfache Neutronenaktivierungsmethode zur Bestimmung von Kupfer in Pflanzenblättern wurde entwickelt. Die bestrahlten Proben werden in Gegenwart von Kupfer-Trägerlösung in einem Gemisch aus rauchender Salpetersäure, 70%iger Überchlorsäure und konzentrierter Schwefelsäure gelöst. Das Kupfer in dieser Losung wird als Kupferronat in Chloroform extrahiert und in konzentrierte Ammoniaklösung zurückextrahiert. Es wird mit 3%iger wäßriger Thioacetamidlösung als Sulfid gefällt und der Niederschlag in Salpetersäure gelöst. Die Kupfer-64-Aktivität in dieser Lösung wird mit einem 400-Kanal-Analysator gezählt. Der Photopeak von Kupfer-64 bei 0,51 MeV wird mit dem eines gleich behandelten Kupferstandards verglichen. Nach dem Zählen wird die chemische Ausbeute an abgetrenntem Kupfer ermittelt durch nochmaliges Bestrahlen von abgemessenen Teilen der Kupfernitratlösung und Vergleich der Kupfer-66-Aktivitat bei 1,04 MeV mit einem weiteren ebenso behandelten Standard. Der Zeitaufwand fur die Analyse einschließlich zweiter Bestrahlung und allen Aktivitätsmessungen beträgt etwa 25 min. Die Genauigkeit der Methode wure geprüft durch Analyse eines biologischen Standards von bekanntem Kupfergehalt. Die vorgeschlagene Methode wurde mit Erfolg auf die Bestimmung von Kupfer in den Blättern 10 verschiedener Pflanzen angewandt (Kupfergehalt 4–30 ppm).

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ANION-EXCHANGE SEPARATION OF METAL IONS IN DIMETHYL SULPHOXIDE–METHANOL–HYDROCHLORIC ACID*

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Summary—The effect of dimethyl sulphoxide on the anion-exchange behaviour of many metals in a methanolic system with hydrochloric acid was explored. Distribution coefficients for 26 elements were determined in a mixed solvent system of dimethyl sulphoxide–methanol–0·6*M* hydrochloric acid, in which the proportions of dimethyl sulphoxide and methanol were varied. Lead(II) and silver(I) complexes are soluble in this system. Interesting effects were noted for gold(III), iron(III), molybdenum(VI) and uranium(VI). As a measure of the usefulness of the systems studied, 27 anion-exchange separations of two- to four-component mixtures of metal ions were carried out, each with quantitative results.

ANION-exchange, especially in systems containing hydrochloric acid, has found extensive application for separations of metal ions. Although useful separations may be obtained in aqueous solutions, several authors have demonstrated the advantages and increased scope of separations made possible through the use of organic solvents.[1–13] Of the various organic solvents used in systems involving hydrochloric acid, methanol has much to recommend it. Equilibrium is usually established more quickly in methanol than in most higher alcohols. Methanol is a fairly good solvent for most metal chlorides, is miscible with water and is easily removed by evaporation following a separation. Finally, a study of 23 metal ions in 0·3 or 0·6*M* hydrochloric acid in methanol showed that all of the elements studied fall into two general groups.[13] One group of metal ions has high distribution coefficients and the elements are strongly retained by an anion-exchange column; the metal ions in the other group all have low distribution coefficients and pass rapidly through an anion-exchange column.

In the present research a comprehensive study was made of the effect of dimethyl sulphoxide (DMSO) on the anion-exchange of metal ions in solutions containing a metal ion, 0·6*M* hydrochloric acid, and varying proportions of methanol and dimethyl sulphoxide. The unusually strong solvating effect of dimethyl sulphoxide on metal chloride complexes has resulted in some interesting, unique and useful ion-exchange effects. For example, lead(II) and silver(I) chloride complexes are sufficiently soluble in DMSO–methanol–hydrochloric acid to permit separation of macro quantities of these elements on ion-exchange columns. The use of a fairly new, highly porous anion-exchange resin permits more rapid equilibration in non-aqueous solvents and enhances the convenience of the separations reported.

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* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 2170.

EXPERIMENTAL

Reagents

Ion-exchange resin. Amberlyst XN-1001 macroreticular anion-exchange resin (Rohm and Haas Company, current designation Amberlyst A-26) was used throughout this study. The active sites for anion-exchange in this resin and in all other strongly basic anion-exchange resins are quaternary ammonium groups. It was ground in a Waring blender and sieved to 60–100 mesh before use. The anion-exchange resin was regenerated as follows: the resin (~150 g) in a large diameter column (8 5 cm) was first back-washed with distilled water to remove any fine particles. The resin was then washed with 2 l. of 2·5 *M* perchloric acid to remove metal ions, after which it was rinsed with water and converted into the chloride form by washing successively with 2 l. of 2 5 *M* hydrochloric acid and with 2 l. of 1·0*M* hydrochloric acid. The resin was rinsed with water, then with absolute ethanol and finally with acetone, after which it was air-dried on filter paper for 24 hr. For column experiments the air-dried resin was soaked in the eluting solution prior to its addition to the column. It was added to the column as a slurry in the eluting solution and washed with about 30 ml of this solution prior to the addition of metal samples

Organic solvents. J. T. Baker purified methanol, absolute ethanol and acetone, and Matheson Coleman and Bell white-label methyl sulphoxide (anhydrous) were used throughout this work.

Organic solvent–hydrochloric acid mixtures. The mixtures were made by adding concentrated hydrochloric acid to the appropriate amounts of organic solvents. The mixture compositions were expressed as % v/v of one organic constituent in terms of the total volume of the organic solvents, and molarity of the hydrochloric acid.

Metal ions investigated. All cations for this investigation, except molybdenum(VI), zirconium(IV), silver(I), indium(III), uranium(VI), thorium(IV) and vanadium(IV), were used as reagent-grade chloride salts. Molybdenum was used as ammonium molybdate; uranium, silver, and thorium as the nitrates; vanadium as the sulphate ($VOSO_4$); indium as the chloride prepared from metallic indium. Zirconium was obtained as hafnium-free zirconyl chloride ($ZrOCl_2$) from the Ames Laboratory of the U.S. Atomic Energy Commission.

Radioactive metal sample. Radioactive silver(I) ($^{110m-110}Ag$; 260-day half-life) was obtained from Oak Ridge National Laboratory in the form of silver(I) nitrate in 3*M* nitric acid.

Metal ion solutions. Solutions for distribution coefficient measurements were prepared with metal concentrations of 0·05*M* by dissolving the metal salts in either dimethyl sulphoxide or methanol and sufficient hydrochloric acid to effect solution being added if necessary. Metal solutions used for most column separations were prepared by dissolving the metal salts in 50% dimethyl sulphoxide–methanol –0·6*M* hydrochloric acid so that the metal ion concentration was 0·01*M*.

Analytical procedures

Most metal ions were determined by titration with 0 01–0 05*M* EDTA by standard titrimetric methods.

Uranium(VI) was determined spectrophotometrically (at 428 mμ) in 30% dimethyl sulphoxide–methanol–0·6*M* hydrochloric acid as its yellow complex with dimethyl sulphoxide.

Silver(I) and molybdenum(VI) were determined by flame emission spectroscopy. All samples were submitted to Analytical Services Group II of the Ames Laboratory for analysis. Silver was determined in solutions of 30% dimethyl sulphoxide–methanol–0·6*M* hydrochloric acid by use of an oxy-hydrogen flame. The emission line used for analysis was 3386 Å. Molybdenum was determined in solutions of 30% dimethyl sulphoxide–methanol–0·6*M* hydrochloric acid by use of a fuel-rich oxy-acetylene flame. The analysis line was 3978 Å.

Gold(III) was determined by atomic-absorption spectroscopy. Samples in 30% dimethyl sulphoxide–methanol–0·6*M* hydrochloric acid were submitted to Analytical Services Group I of the Ames Laboratory for analysis. A gold hollow-cathode lamp was used and absorption measured at a wavelength of 2428 Å.

Silver(I), 260-day half-life, was used in a column study to demonstrate its quantitative elution with concentrated hydrochloric acid. It was added as a tracer in a stock solution of silver chloride and after elution its recovery was determined by comparison of the counts of the recovered sample with those in an identical aliquot taken from the stock solution. The instrument was set at a threshold energy of 0·600 MeV, and a window width of 0·400 MeV was used. The total activity added to the column was 0·25 μC and 2% of this was counted for recovery evaluation.

Distribution coefficients

Distribution coefficients were determined in the following manner: quantities of approximately 1 g of air-dried anion-exchange resin were accurately weighed into 250-ml ground-glass stoppered Erlenmeyer flasks. Then 50 ml of the appropriate solvent mixtures containing 0·20 mmole of the metal ion concerned were transferred by pipette into the flasks. The flasks were tightly stoppered and shaken on a Burrell shaker until equilibrium was attained. Three 10-ml aliquots were taken of the liquid phase which had been filtered free from resin, and these were analysed for the metal ion present. Distribution coefficients were calculated in terms of the weight of the air-dried resin and then corrected once the weight-loss of the air-dried resin on heating at 110° for 2 hr had been determined. The resin was found, generally, to lose 9% of its weight on drying.

In order to determine the time period required for equilibration of a metal solution with the resin phase, a kinetic study was made, using copper(II) as a representative element. Distribution coefficients of copper(II) in 20% dimethyl sulphoxide–methanol–0·6*M* hydrochloric acid were determined as a function of equilibration time. From this study an equilibration time of 2 hr was chosen for all distribution studies.

Column separation procedure

To prepare an ion-exchange column the air-dried resin was first slurried in a beaker with the solvent mixture being used, and the slurry was then added to a glass column to the desired height. A glass-wool plug was used to support the resin in the column. For most separations a column height of 8 cm was used. About 30 ml of the solvent mixture were then passed through the column at a moderate flow-rate to ensure the attainment of equilibrium and also to help settle the resin. A glass-wool plug was placed at the top of the resin bed to help stabilize the resin when samples and eluents were added. The metal ion sample mixture was prepared by adding 5 ml of each metal solution (in the first eluting solvent) to the column by pipette. The mixture was passed through the resin at a flow-rate of 1 ml/min, and the first component was eluted, usually by passing an additional 15 ml of the eluting solvent through the column at the same flow-rate of 1 ml/min. After elution of the first metal the eluent was changed to elute the second component. It was never necessary to reduce the flow-rate below 1 ml/min to effect any of the separations performed.

RESULTS

Conventional anion-exchange resins are gel-like and often swell or shrink considerably when the composition of the eluting solvent is altered. Furthermore, the rate of exchange for these resins is often considerably slower in organic solvents than in water. This usually necessitates a slow flow-rate for column separations in non-

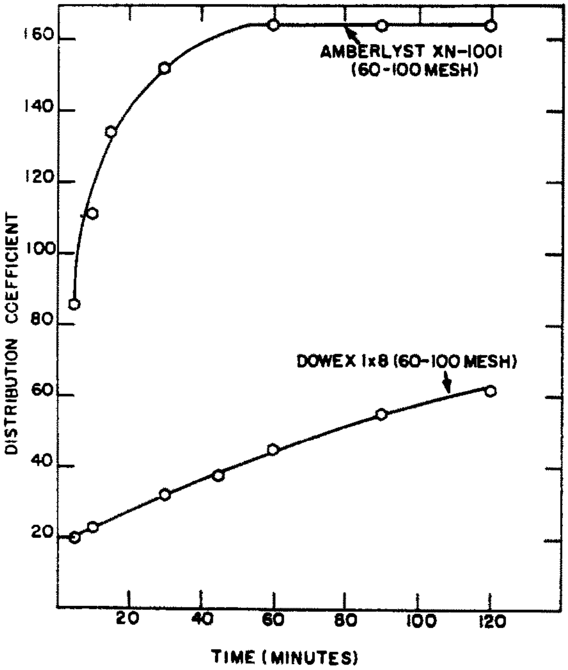

FIG. 1.—Comparison of the equilibration rates of copper(II) with Amberlyst XN-1001 and Dowex 1 × 8 anion-exchange resins in 30% dimethyl sulphoxide–methanol–0·6*M* hydrochloric acid.

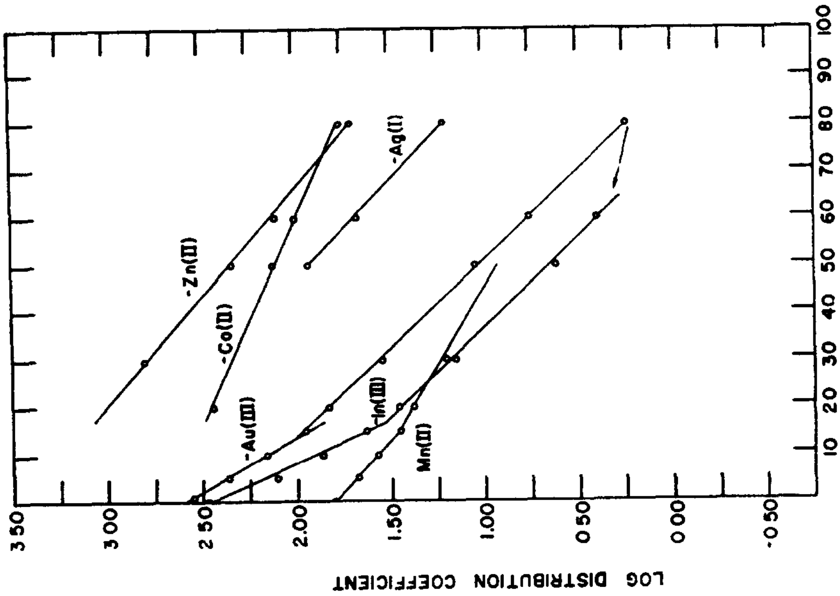

FIG. 3.—Anion-exchange distribution coefficients of metal ions in dimethyl sulphoxide–methanol–0 6*M* hydrochloric acid.

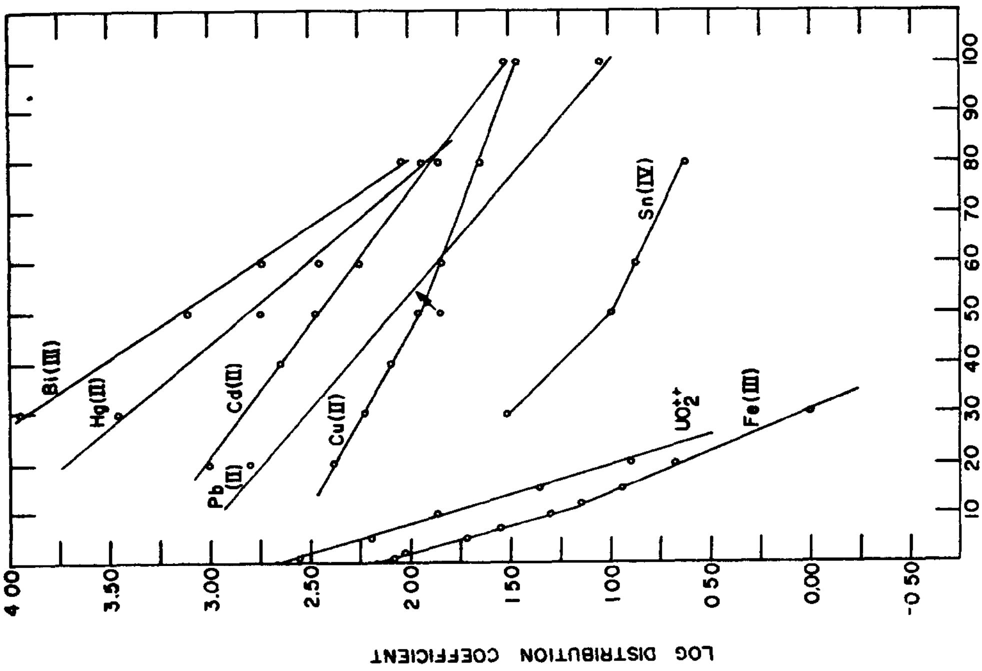

FIG 2.—Anion-exchange distribution coefficients of metal ions in dimethyl sulphoxide–methanol–0 6*M* hydrochloric acid

aqueous solvents. The "macroreticular" resins recently developed are characterized by large pores (several hundred Å) which permeate the spherical beads.[14] This pore system is retained in the dry state as well as when the resin is mixed with a solvent, and the resin does not swell or shrink appreciably.

The macroreticular resin used in this work is Amberlyst XN-1001 (current designation A-26). The more rapid equilibration rate of this resin is demonstrated in Fig. 1 for copper(II) in DMSO–methanol–0·6*M* hydrochloric acid equilibrated with this resin, and in a separate experiment with a conventional anion-exchange resin. In this particular case, the equilibrium value of the distribution coefficient is considerably higher for the Amberlyst than for the other resin.

Distribution coefficients for 26 elements, measured in 0·6*M* hydrochloric acid in varying proportions of dimethyl sulphoxide and methanol, are presented graphically in Figs. 2 and 3 and in Table I for the elements with low distribution coefficients

TABLE I —DISTRIBUTION COEFFICIENTS OF METAL IONS ON AMBERLYST XN-1001 FROM DIMETHYL SULPHOXIDE–METHANOL–0·6*M* HYDROCHLORIC ACID

Metal ion	Distribution coefficient			
	30% DMSO	50% DMSO	60% DMSO	80% DMSO
Al(III)	~0	~0	~0	—
Ca(II)	~0	~0	~0	<1
Mg(II)	~0	~0	~0	<1
Mo(VI)	~0	~0	~0	~0
Ni(II)	0·48	0·83	0·94	1·2
Sr(II)	~0	~0	~0	<1
Th(IV)	~0	~0	~0	~0
Ti(IV)	0·03	0·16	0·26	0·41
V(IV)	~0	~0	~0	~0
Zr(IV)	0·12	0·12	—	—

Roughly the elements studied divide themselves into three groups. One group of metal ions is rather strongly retained by the anion-exchange resin from all compositions of methanol and DMSO. A second group, listed in Table I, is either not retained or is only slightly retained by the resin. A third group consists of metal ions which have high distribution coefficients in methanol but very low distribution coefficients in methanol-DMSO containing a significant proportion of DMSO. This group includes gold(III), iron(III), uranium(VI) and probably indium(III) and molybdenum(VI).

Lowering of the distribution coefficient of gold(III) by DMSO is useful because it permits gold(III) to be eluted from an anion-exchange column in dilute hydrochloric acid solution. (This was confirmed by actual column experiment.) With conventional anion-exchange resins, gold(III) has an extremely high distribution coefficient (up to 10^6) and is almost impossible to remove from the column. In this connection the suggestion of Burstall[15] of using acetone to remove gold from an anion-exchange column is pertinent. It appears, however, that dimethyl sulphoxide is more efficient than acetone for this purpose.

The much lower distribution coefficients of iron(III), molybdenum(VI), uranium(VI) and indium(III) in solvents containing dimethyl sulphoxide is unusual because published studies indicate that the anion-exchange coefficients of these metals in alcohols and other organic solvents containing hydrochloric acid are generally quite high. Korkisch and Hazan[13] did note that iron(III) and indium(III) have abnormally low distribution coefficients in acetone–hydrochloric acid, and they used this effect to separate iron(III) from cobalt(II) and nickel(II).[16] However, they found a distribution coefficient in excess of 100 for uranium(VI), whereas our data show very low distribution coefficients for uranium(VI) in methanol-DMSO.

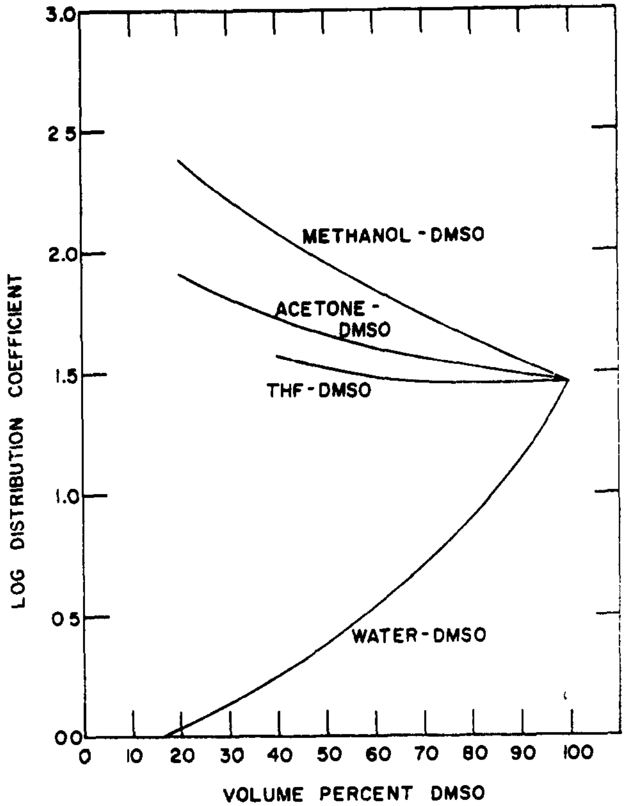

Fig. 4.—Distribution coefficients of copper(II) on Amberlyst XN-1001 as a function of solvent composition in solvent systems containing 0·6*M* HCl and varying proportions of DMSO and another solvent.

Dielectric constants for pure solvents: dimethyl sulphoxide, 48·9; methanol, 32·6; acetone, 20·7; tetrahydrofuran, 8·0.

The distribution coefficients for copper(II) were compared for several dimethyl sulphoxide binary solvent mixtures, each containing 0·6*M* hydrochloric acid (Fig. 4). As seen from the dielectric constants of the pure solvents (given in the figure caption) there is no apparent relationship between the exchange behaviour and the dielectric constant for these solvents.

Several other elements were studied in water–DMSO–0·6*M* hydrochloric acid. The results in Fig. 5 show that while the distribution coefficients for copper(II) and

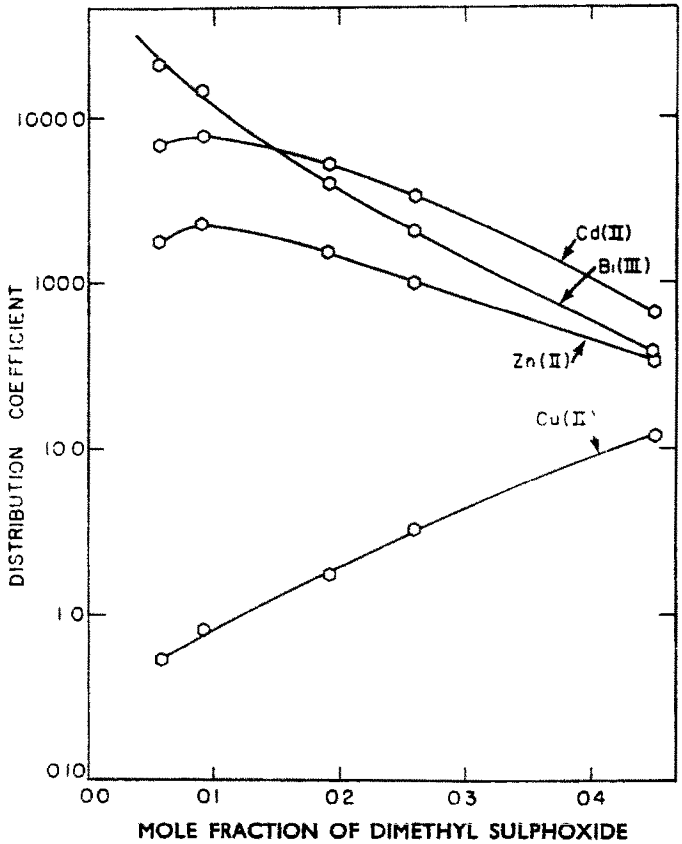

FIG. 5.—Distribution coefficients of four metals chlorides as a function of the mole fraction of dimethyl sulphoxide in a system of dimethyl sulphoxide–water–0·6*M* hydrochloric acid on Amberlyst XN-1001 resin.

cobalt(II) decrease with increasing proportions of water the distribution coefficients of bismuth(III), cadmium(II) and zinc(II) are actually higher in the solvent mixtures containing higher proportions of water. This means that bismuth(III), cadmium(II) and zinc(II) may be separated from copper and cobalt(II) in water–DMSO–hydrochloric acid.

A study of the effect on metal distribution coefficients of increasing the hydrochloric acid concentration (and hence increasing the water content also) in 20% DMSO–80% methanol is given in Table II. It was hoped that this might result in a significant increase in the distribution coefficients of titanium(IV) and zirconium(IV). However, the results approximate ion-exchange behaviour in aqueous solutions containing a high concentration of hydrochloric acid, and no significant advantage is seen for the use of dimethyl sulphoxide and methanol over the aqueous system at high acidities.

The ultimate test of the usefulness of a new system for ion-exchange chromatography lies in its applicability to actual column separations. Accordingly quantitative separation and analysis of some 27 mixtures containing from two to four different elements in each were performed. The data given in Table III are representative of the quantitative separations obtained; space does not permit a complete listing.

TABLE II.—DISTRIBUTION COEFFICIENTS FOR FIVE METALS ON AMBERLYST XN-1001 RESIN FROM 20% DIMETHYL SULPHOXIDE–METHANOL–HYDROCHLORIC ACID SOLUTIONS AS A FUNCTION OF ACID STRENGTH

[HCl]	Co(II)	Pb(II)	Ti(IV)	Zr(IV)	Fe(III)
1·21*M* (10%)	426	747	~0	~0	6·5
2·42*M* (20%)	293	338	~0	~0	16
3·62*M* (30%)	211	168	~0	~0	47
4·85*M* (40%)	155	67	~0	~0	142
6·05*M* (50%)	117	22	0·39	~0	443
7·25*M* (60%)	87	7·0	0·80	1·6	1631
8·45*M* (70%)	71	3·2	1·9	6·5	5426
8·65*M* (72%)	—	—	—	8·4	—
9·07*M* (75%)	61	1·9	3·0	—	—

With few exceptions, the recoveries obtained are within the limits of expected error for the titration conditions employed.

The merits of the solvent system and resin used for these separations are impressive. Many elements are included in the separation scheme. Even for resolution of four-component mixtures, a column length of 10 cm proved totally adequate, because under the conditions of elution metals not eluted remain in tight bands at the top of the column until the eluent is changed to elute the next element. The flow-rate of the eluent through the column was at no time less than 1 ml/min, which is a considerable improvement over existing methods which generally allow a flow-rate of 0·5 ml/min or less for the same diameter column. Elution curves for the elements are symmetrical and show no tailing (see Fig. 6). Application of elementary plate theory to this curve gave 36 theoretical plates for the 8·9-cm column, which corresponds to an HETP of 0·25.

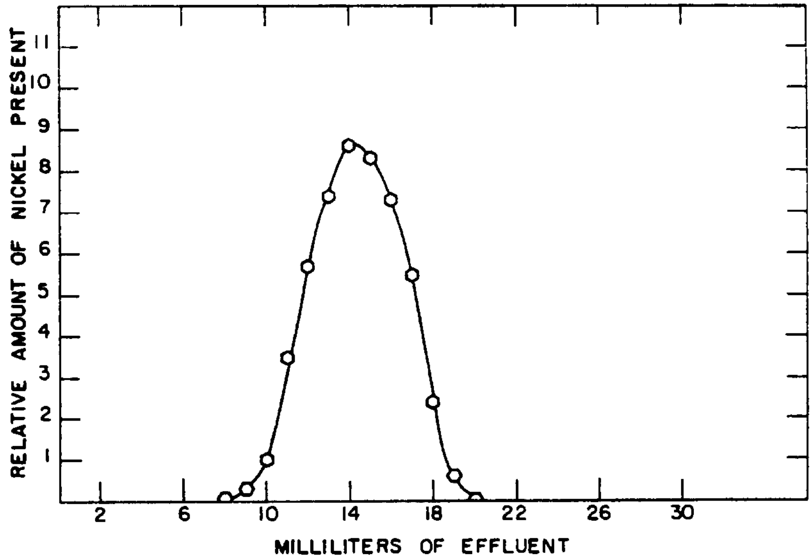

FIG. 6.—Elution curve for nickel(II) from an 8·9-cm column of Amberlyst XN-1001 resin, using 50% dimethyl sulphoxide–methanol–0·6*M* hydrochloric acid.

TABLE III.—TYPICAL SEPARATIONS USING A COLUMN PACKED WITH 60–80 MESH AMBERLYST XN-1001 AND DIMETHYL SULPHOXIDE–METHANOL–HYDROCHLORIC ACID AS THE PRIMARY ELUENT

Ions separated	Eluent		Column	Added,	Found,	Error, %
	Composition	Volume, *ml*	length, cm	*mmoles*	*mmoles*	
Zr(IV)	50% DMSO–MeOH–0.6*M* HCl	40	9	0.0536	0.0532	−0.8
Pb(II)	8*M* HCl	40	—	0.0476	0.0477	+0.2
Ni(II)	50% DMSO–MeOH–0.6*M* HCl	30	9	0.0559	0.0560	+0.2
Bi(III)	1*M* H_2SO_4	70	—	0.0497	0.0498	+0.2
Mo(VI)	50% DMSO–MeOH–0.6*M* HCl	30	9	0.0500	0.0500	0.0
Pb(II)	8*M* HCl	50	—	0.0483	0.0483	0.0
Co(II)	DMSO–80% H_2O–0·6*M* HCl	30	7.5	0.0527	0.0528	+0.2
Bi(III)	1*M* H_2SO_4	70	—	0.0485	0.0485	0.0
Co(II)	DMSO–80% H_2O–0.6*M* HCl	30	7.5	0.0528	0.0527	−0.2
Pb(II)	8*M* HCl	50	—	0.0494	0.0494	0.0
Zr(IV)	20% DMSO–MeOH–4.85*M* HCl	25	7.5	0.0535	0.0537	+0.4
Mo(VI)	50% DMSO–MeOH–0.6*M* HCl	30	—	0.0500	0.0502	+0.4
Ni(II)	50% DMSO–MeOH–0.6*M* HCl	50	13	0.7324	0.7321	0.0
Pb(II)	8*M* HCl	50	—	0.0854	0.0853	−0.1
Ni(II)	50% DMSO–MeOH–0.6*M* HCl	30	10	0.7500	0.7500	0.0
Pb(II)	8*M* HCl	40	—	1.0340	1.0340	0.0
Co(II)	1*M* HCl	30	—	1.1060	1.1000	−0.5
Bi(III)	1*M* H_2SO_4	80	—	1.0580	1.0560	−0.2

DISCUSSION

It is interesting and useful that lead(II) and silver(I) are included in the separation scheme given here. More than trace amounts of these elements cannot be separated by anion-exchange in other non-aqueous solvents because lead chloride and silver chloride precipitate. In solvents containing DMSO, the equilibrium

$$AgCl(s) + xCl^- \rightleftharpoons (AgCl_{x+1})^{x-}$$

is apparently shifted to the right because of strong solvation by DMSO. Solubilization of uncharged silver chloride by DMSO solvation is less likely because Ag^+ and Cl^- in an approximately 1:1 mole ratio results in precipitation even in DMSO. Excess of chloride, however, dissolves the precipitate. Lead(II) probably forms an anionic chloride complex solvated by DMSO in some similar manner to the silver(I).

The question arises as to how we may explain the facts, (*a*) that many metal ions are sorbed strongly by anion-exchange resins in organic solvents that contain a much lower concentration of chloride than is required for their uptake from aqueous hydrochloric acid, and (*b*) that DMSO greatly decreases the uptake of iron(III), uranium(VI), *etc.* while maintaining a strong uptake of other metal ions such as copper(II) and zinc(II). The following explanations appear reasonable.

(*a*) Organic solvents in general make it easier to strip co-ordinated water from a metal cation and form a metal–chloride complex.[1] The fact that these metal chloride complexes do form at low hydrochloric acid concentrations in organic solvents is evident from visible spectra in several instances. The metal chloride complexes formed may then be taken up by the anion-exchange resin. This may occur by simple ion-exchange of the anionic metal chloride complex, or a neutral metal chloride complex may invade the resin and form an anionic complex inside the resin by reaction with additional chloride ions.

(*b*) Solvation of the metal chloride complex by the solution outside the resin competes with the process by which the metal complex is taken into the resin phase. Ordinarily uptake by the resin predominates, but an unusually strong solvating effect may cause the metal complex to remain mostly in the solution phase outside the resin. Apparently the latter occurs with iron(III), uranium(VI), molybdenum(VI), gold(III), *etc.*, when DMSO is present. Dimethyl sulphoxide is known to form complexes with certain metal salts. Also, Korpak[17] showed that a higher dialkyl sulphoxide, dioctyl sulphoxide, causes the extraction of UO_2Cl_2 or $UO_2(NO_3)_2$ into an indifferent organic solvent by solvation of the neutral uranyl species.

The best way to plot distribution coefficients as a function of solvent composition is open to question. Plots of log *D vs.* log mole fraction of dimethyl sulphoxide are linear for most of the elements studied between 20% and 80% of dimethyl sulphoxide but are curved at low concentrations of DMSO. The plots of log *D vs.* % v/v DMSO are mostly linear and are perhaps more clear for visual display of results.

Zusammenfassung—Der Einfluß von Dimethylsulfoxid auf das Anionenaustauschverhalten mehrerer Metalle in einem salzsauren Methanolmedium wurde untersucht. Die Verteilungskoeffizienten fur 26 Elemente wurden in einem Mischlosungsmittelsystem Dimethylsulfoxid-Methanol-0,6*M* Salzsaure ermittelt, wobei die Anteile an

Dimethylsulfoxid und Methanol variiert wurden. Blei(II)- und Silber(I)-Komplexe sind in diesem System loslich. Interessante Effekte wurden bei Gold(III), Eisen(III), Molybdan(VI) und Uran(VI) gefunden. Als Maß fur den Nutzen der untersuchten Systeme wurden 27 Anionenaustauschtrennungen von binaren bis quaternaren Gemischen von Metallionen ausgeführt, jeweils mit quantitativen Ergebnissen.

Résumé—On a examiné l'effet du diméthylsulfoxyde sur le comportement d'échange d'anions de nombreux métaux dans un système méthanolique avec de l'acide chlorhydrique. On a déterminé les coefficients de partage pour 26 éléments dans un système de solvants mélangés constitué de diméthylsulfoxyde-méthanol-acide chlorhydrique 0,6M, dans lequel on a fait varier les proportions de diméthylsulfoxyde et de méthanol. Les complexes du plomb(II) et de l'argent(I) sont solubles dans ce système. On a noté des effets intéressants pour l'or(III), le fer(III), le molybdène(VI) et l'uranium(VI). Pour évaluer l'utilité des systèmes étudiés, on a réalisé 27 séparations par échange d'anions de mélanges d'ions métalliques contenant deux à quatre constituants, chacune avec des résultats quantitatifs.

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DIE ANWENDUNG VON KOMPLEXBILDNERN IN DER POLAROGRAPHISCHEN ANALYSE ANORGANISCHER VERBINDUNGEN—XIII*

POLAROGRAPHISCHES VERHALTEN DER KOMPLEXVERBINDUNGEN DES MANGANS MIT MANNIT

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Zusammenfassung—Es wurde das polarographische Verhalten der Komplexbildung von Mangan mit Mannit in alkalischer Lösung studiert, und festgestellt, daß das Mangan(II)-hydroxid mit Sauerstoff oder Wasserstoffperoxid zum braungefärbten Mangan(III)-Mannit Komplex und weiter zum rotgefärbten Mangan(IV)-Mannit Komplex oxidiert wird. Das System Mangan(III)-Mannit → Mangan(IV)-Mannit verhält sich an der D.M.E. wie ein reversibles Redoxsystem mit $E_{1/2} = -0{,}375$ V. Das wahrscheinliche Reaktionschema wird diskutiert. Mangan, bis 10^{-4} Mol/l., in Gegenwart eines 20-fachen Überschusses von Kupfer in einer Lösung die 3 Mol/l Kaliumhydroxid und 0,5 Mol/l Mannitol enthält polarographisch bestimmt werden. Bei Anwesenheit von Ethylendiamin (0,5 Mol/l.) stören weder Kobalt noch Eisen(III). Die $E_{1/2}$-werte von 21 Kationen in diesem Electrolyten werden angegeben. Die Methode wurde für die Bestimmung von Mangan in Dolomiten und Schiefergestein verwendet.

IM Rahmen der systematischen polarographischen Grundlagenforschung wurden chelatbildende Eigenschaften von Verbindungen mit den Atomen N,N (Äthylendiamin und dessen Salze), N,O (Glycin, Glutaminsäure, Aminopolyalkohole) und O,O (Benzcatechindisulfonsäure) untersucht.

In der Literatur wurde bisher das polarographische Verhalten der Komplexverbindungen des zwei- und dreiwertigen Eisens mit Mannit[1] und Saccharose[2] beschrieben. Eine alkalische Mannit-Lösung wurde von Perkins und Reynolds[3] für die polarographische Bestimmung von Chromat(VI) und Eisen(III) verwendet. Mit der polarographischen Bestimmung von Mangan, Kupfer, Chrom und Eisen in unlöslichen Rückständen, die beim Lösen von metallischem Calcium in Salzsäure erhalten werden, beschäftigten sich Reynolds und Shalgosky in einer weiteren Mitteilung.[4] Dabei versuchten die Autoren den wahrscheinlichen Reaktionsprozeß der Manganreduktion an der Quecksilbertropfelektrode zu deuten und führten folgende Gleichung an:

$$\mathrm{Mn^{III}\text{-}Komplex} \rightarrow \mathrm{Mn^{II}\text{-}Komplex}$$

Mit dem gleichen Problem beschäftigte sich Skokan.[5]

In der vorliegenden Arbeit werden die Ergebnisse der polarographischen, volumetrischen und spektrophotometrischen Studien der Komplexverbindungen des Mangans mit Mannit in alkalischem Medium mitgeteilt. Gleichzeitig wird versucht die an der Quecksilber-Tropfelektrode im genannten Medium ablaufenden Redox-Vorgänge des Mangans mit Hilfe eines Reaktionschemas zu deuten.

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* Mitteilung XII: J. Doležal, V. Petrus and J. Zýka, *J. Electroanal. Chem.*, 1962, 3, 274.

EXPERIMENTELLER TEIL

Reagenzien

Der Titer der für die Versuche verwendeten 0,1 m Mangan(II) sulfatlösung (Präparat der Firma Merck, *p.a.*) wurde komplexometrisch und gravimetrisch ermittelt.

Die für die Versuche verwendete Mannitlösung wurde durch Auflösen von 18,22 g Mannit (Präparat rein, der Firma VEB Berlin-Chemie) in 100 ml redestilliertem Wasser hergestellt.

Weiter wurde eine 6 m Kaliumhydroxidlösung (Präparat *p.a.* der Firma Lachema) verwendet.

Alle übrigen Reagenzien waren durchwegs vom Reinheitsgrad *p.a.* Für die jodometrische Manganbestimmung wurde eine genau eingestellte 0,01 n Natriumthiosulfatlösung verwendet. Zur potentiometrischen Manganbestimmung diente eine genau eingestellte 0,1 n Kaliumhexacyanoferrat(III)-lösung.

Apparatur

Fur die polarographischen Messungen wurde durchwegs ein Polarograph PO 4 (Firma Radiometer Kopenhagen) verwendet. Als Reagenzgefäß diente ein Gefäß nach Kalousek mit Dreiweghahn und gesättigter Kalomel-Elektrode. Der Durchmesser des Quecksilberbodens betrug *ca.* 4 cm. Die Kapillar-Tropfzeit bei einer Reservoirhöhe von 49 cm betrug $t = 3$ sec.

Bei allen Versuchen wurde eine vollkommen inerte Atmosphäre durch Verwendung von reinst Stickstoff, hergestellt in einer Apparatur nach Meyer und Ronge,[8] geschaffen. Mit diesem, stets durch die genannte Apparatur geleiteten Stickstoff wurde die Elektrolyt- und Reagenzlösung vor der Reaktionsmessung 10 min durchblasen. Während der polarographischen Messung wurde der Stickstoff mittels eines Zweiweghahns über die Reaktionslösung hinweggeführt. Alle Messungen wurden bei 20° durchgeführt (das Kalousek-Gefäß konnte mit einem Thermostat temperiert werden).

Für die potentiometrischen Messungen wurde ein Autotitrator der Firma Radiometer Kopenhagen verwendet. Die inerte Atmosphäre wurde wie bei den polarographischen Messungen geschaffen. Die volumetrischen Messungen wurden mit Hilfe von 10-ml Büretten durchgeführt.

Alle Absorptionsspektren wurden mit dem Spektralphotometer Unicam SP 800 aufgenommen.

ERGEBNISSE

Polarographisches Verhalten von Mangan in alkalischer Mannitlösung

Bei der Verwendung alkalischer Mannitlösungen für die polarographische Bestimmung von Schwermetallionen fanden wir beim Mangan, im Gegensatz zu den Ergebnissen von Reynolds und Shalgosky,[4] in 3 m Kaliumhydroxid- und 5%iger Mannitlösung in inerter Atmosphäre keine gut ausgeprägte anodische Stufe, sondern eine Doppelstufe, die für analytische Zwecke nicht ausreichend reproduzierbar ist (Abb. 1).

Zur Klärung des Auftretens dieser Mangan-Doppelstufe wurde ein größerer alkalischer Mannit-Bereich in Gegenwart von Mangan(II) polarographisch abgetastet. Dazu wurden jeweils 0,05; 0,1; 0,25 und 0,5 m Mannitlösungen mit den Kaliumhydroxidkonzentrationen 0; 0,05; 0,1; 0,5; 1,0; 2,0 und 3,0 m variiert und als Leitelektrolyt verwendet. Die eingesetzte Mangankonzentration betrug $5{,}45 \,.\, 10^{-3}$ m. Hierzu muß betont werden, daß in inerter Atmosphäre bei Zugabe der Mangan(II)-Lösung zur alkalischen Mannitlösung stets ein flockiger Niederschlag von Manganhydroxid zu beobachten war. Die Ergebnisse der vier Versuchsserien sind in der Tabelle I ersichtlich. Die gemessenen Tabellenwerte sind mit einem relativen Fehler von $\pm 5\%$ behaftet.

Der Tabelle ist zu entnehmen, daß mit abnehmender Hydroxid- bzw. Mannitkonzentration das Halbstufenpotential der positiver gelegenen Stufe zu positiveren Werten (von −0,375 bis −0,240 V) verschoben wird, während das der negativer gelegenen Stufe sich nur unwesentlich verändert (von −0,61 bis −0,58 V). Mit der Verschiebung der Halbstufenpotentiale bei abnehmenden Hydroxid- bzw. Mannitkonzentrationen verringert sich auch die Stufenhöhe der Doppelwelle, deren positiver gelegene Stufe in einer Lösung mit einem Mannit- bzw. Hydroxidgehalt von 0,05 bzw.

0,1 m nur noch angedeutet erscheint. Die negativer gelegene Stufe der Doppelwelle verschwindet bereits bei einem Mannit- bzw. Hydroxidgehalt unterhalb 0,1 bzw. 1,0 m.

Die erzielten Ergebnisse sind nur in absolut inerter Atmosphäre mit dem angeführten Fehler reproduzierbar, andernfalls löst sich der Manganhydroxid-Niederschlag auf und die Lösung färbt sich infolge der Oxydation von Mangan(II)-Hydroxid durch Luftsauerstoff braun. Bei der polarographischen Aufzeichnung dieses Oxydationsvorganges tritt die negativer gelegene Stufe nicht mehr auf. Dagegen entsteht die positiver gelegene Stufe in gut ausgeprägter und reproduzierbarer Form beim gleichen Halbstufenpotential von —0,375 V. Wenn man die Oxydation der Lösung, die 3,0 m Kaliumhydroxid, 0,5 m Mannit und 5,45 . 10^{-3} m Mangan(II)-Ionen enthält, mit Sauerstoff durchführt, so durchläuft die anodische Stufe ($E_{1/2}$ = —0,375 V) die Galvanometer-Nullinie und nach einem einstündigen Einleiten von Sauerstoff erhält man nur noch eine kathodische Stufe mit dem Halbstufenpotential $E_{1/2}$ = —0,380 V. Die Lösung färbt sich dabei über dunkelbraun nach rubinrot.

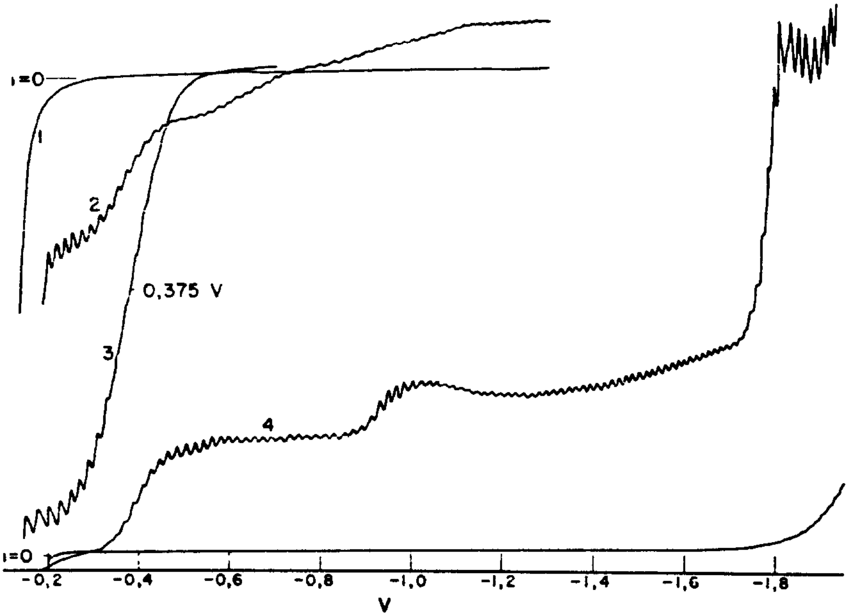

Abb. 1.—Polarographisches Verhalten von Mangan in alkalischer Mannitlösung. Kurve 1: 3 m KOH, 0,5 m Mannit in inerter Atmosphäre; Kurve 2: wie 1, mit 5,45 . 10^{-3} m Mn^{++}; Kurve 3: wie 2, nach 20 Sek. Oxydation mit O_2 (5 Min N_2); Kurven 1, 2, 3 mit Empf. 15 μA. Kurve 4: wie 2, nach Oxydation mit O_2 (90 Min.) und danach 10 Min. Stickstoff. Empfindlichkeit: 70 μA.

Aus der Tabelle ist weiterhin ersichtlich, daß bei Verminderung der Hydroxidkonzentration bei konstantem Mannitgehalt das Halbstufenpotential der Redox-Stufe zu positiveren Werten verschoben wird. Die Stufenhöhe bleibt dabei konstant. Verringert man die Mannitkonzentration bei konstant bleibendem Hydroxidgehalt, so verändert sich weder das Halbstufenpotential noch die Stufenhöhe der Redox-Stufe. Sowohl die Redox- als auch die kathodische Stufe ist am besten ausgeprägt in einer Lösung, die 0,5 m Mannit und 3,0 m Kaliumhydroxid enthält.

Nach der Oxydation mittels Sauerstoff ist die Höhe der kathodischen Stufe gleich der anodischen Stufenhöhe bei konstant bleibendem Halbstufenpotential.

TABELLE I.—POLAROGRAPHISCHE ERGEBNISSE

Mannit *Mol/l*	KOH *Mol/l*	I. $E_{1/2}$ (anod.) *V*	II. $E_{1/2}$ (anod.) *V*	I. i_d *µA*	II. i_d *µA*	I. $E_{1/2}$ (kat.) *V*	= i_d, *µA*	davon i_d (anod.) *µA*
0,5	0	—	—	—	—	—	—	—
	0,05	—	—	—	—	−0,145	9,9	6,7
	0,1	−0,240	—	0,5	—	−0,235	11,9	5,7
	0,5	−0,315	(−0,60)	0,85	0,05	−0,315	11,7	4,4
	1,0	−0,340	−0,60	1,5	0,25	−0,345	11,6	3,3
	2,0	−0,360	−0,61	2,2	0,5	−0,375	11,5	2,7
	3,0	−0,375	−0,61	3,2	0,7	−0,380	11,5	2,1
0,25	0	—	—	—	—	—	—	—
	0,05	—	—	—	—	−0,150	10,1	6,9
	0,1	−0,240	—	0,25	—	−0,235	12,1	4,9
	0,5	−0,310	—	0,8	—	−0,315	12,0	2,0
	1,0	−0,330	−0,60	1,5	0,15	−0,340	12,2	1,1
	2,0	−0,350	−0,61	2,2	0,4	−0,365	11,6	—
	3,0	−0,375	−0,61	2,2	0,5	−0,380	11,5	—
0,1	0	—	—	—	—	—	—	—
	0,05	—	—	—	—	−0,20	10,3	2,3
	0,1	−0,26	—	0,2	—	−0,26	12,0	1,9
	0,5	−0,32	—	0,8	—	−0,325	11,8	—
	1,0	−0,34	—	1,1	—	−0,34	11,9	—
	2,0	−0,355	−0,58	1,3	0,1	−0,36	12,0	—
	3,0	−0,370	−0,58	1,5	0,2	−0,375	11,4	—
0,05	0	—	—	—	—	—	—	—
	0,05	—	—	—	—	−0,25	8,7	0,9
	0,1	−0,26	—	0,2	—	−0,26	11,5	0,6
	0,5	−0,32	—	0,6	—	−0,32	11,7	—
	1,0	−0,34	—	1,1	—	−0,34	11,5	—
	2,0	−0,35	—	1,2	—	−0,35	11,4	—
	3,0	−0,36	—	1,2	—	−0,37	11,4	—

Erläuterungen: I. $E_{1/2}$ (anod.) = Halbstufenpotential der positiver gelegenen Stufe der Doppelwelle.
II. $E_{1/2}$ (anod.) = Halbstufenpotential der negativer gelegenen Stufe der Doppelwelle.
I. $E_{1/2}$ (kat.) = Halbstufenpotential der Redox- bzw. der kathodischen Stufe, erhalten nach 15 Min Einleiten von Sauerstoff.
i_d = gemessener Diffusionsstrom aus den erhaltenen polarographischen Stufen.
Temp. 20°C; Kapillartropfzeit t = 3,5 sec

Die Oxydation der alkalischen Mangan(II)-Mannitlösung läßt sich auch mittels Wasserstoffperoxid durchführen. Die damit erzielten Ergebnisse entsprechen den mit Sauerstoff erhaltenen vollkommen. Die Abhängigkeit der kathodischen und Redox-Stufe von der Wasserstoffperoxidkonzentration ist der Tab. II zu entnehmen. Aus der Tabelle geht hervor, daß bei Zugabe von 0,015 ml 3%iger Wasserstoffperoxidlösung—das ist der nach der Gleichung (IV) berechnete theoretische Wert—die anodische Stufe fast quantitativ entsteht. Bei Zugabe von 0,06 ml tritt bereits ein kathodischer Anteil in Erscheinung, der anzeigt, daß ein Teil des Mangans bereits in die vierwertige Stufe oxydiert wurde, die schließlich bei Zugabe von 0,6 ml quantitativ erreicht wird.

Bei Verwendung von Sauerstoff als Oxydationsmittel werden die gleichen Effekte erzielt. So erhält man die dreiwertige Oxydationsstufe durch Einleiten von Sauerstoff nach *ca.* 3 Sekunden und die vierwertige Manganstufe nach *ca.* einer Stunde. Der überschussige Sauerstoff wird mit Hilfe von eingeleitetem Stickstoff aus der Lösung vertrieben.

Die rubinrote Lösung des vierwertigen Mangan-Mannit-Komplexes verfärbt sich beim Stehen im Tageslicht nach *ca.* 20 Stunden braun. Bei der polarographischen Untersuchung dieses Vorganges stellten wir fest, daß die kathodische Stufe die Galvanometer-Nullinie durchläuft (Redox-Stufe) und nach *ca.* 30 Stunden nur noch als anodische Welle auftritt. Diese Photoreaktion läßt sich durch intensivere Lichteinwirkung beschleunigen. Die Ergebnisse des Reduktionsvorganges im Dunkeln, an der Luft, beim standigen Durchblasen von Stickstoff und bei Verwendung einer Lichtquelle sind in der Abb. 2 veranschaulicht

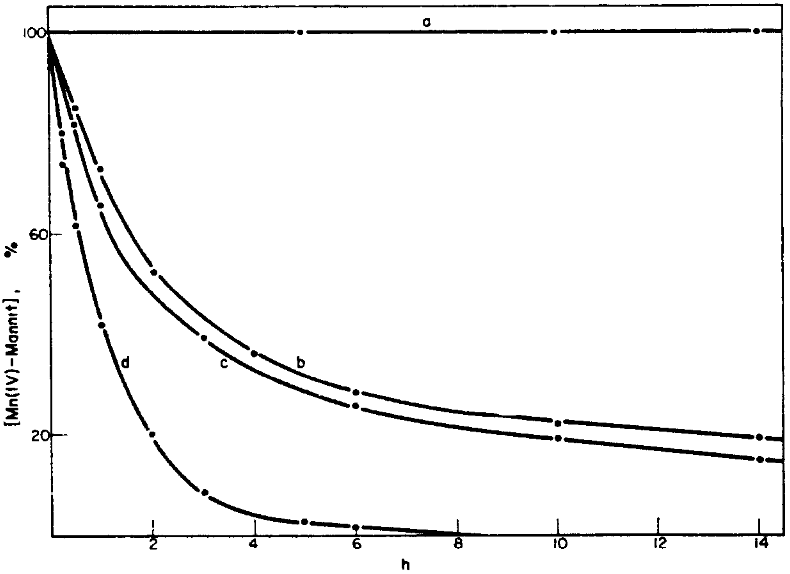

ABB. 2.—Polarographische Untersuchung der Photoreduktion [Mn(IV)-Mannit] → [Mn(III)-Mannit].
In Lösung 3 m KOH, 0,5 m Mannit, 5,45 . 10^{-3} m Mn^{++} wurde 90 Min O_2, dann 10 Min N_2 eingeleitet, dann kathodische Stufe gemessen (*a*) im Dunkeln aufbewahrt, (*b*) im Tageslicht an der Luft, (*c*) bei dauernden Einleiten von N_2, (*d*) bei Verwendung einer 250-Watt-Lichtquelle.

Die Abhängigkeiten der anodischen, anodisch-kathodischen und kathodischen Stufenhöhe von der Quadratwurzel der Reservoirhöhe, sowie von der Mangankonzentration im Bereich von 2 . 10^{-3} bis 1 . 10^{-2} m zeigen direkte Proportionalität. Bei der Polarisation der Quecksilber-Tropfelektrode in einer Lösung von 0,5 m Mannit, 3,0 m Kaliumhydroxid und 5,45 . 10^{-3} m Mangan(II) im erreichbaren Bereich von —0,1 bis —1,85 V erhält man in inerter Atmosphäre die erwähnte anodische Doppelwelle ($E_{1/2}$ = —0,375 und $E_{1/2}$ = —0,61 V) und bei *ca.* $E_{1/2}$ = —1,73 V eine kathodische Stufe. Wird der gleiche Vorgang nach der Oxydation mit Sauerstoff wiederholt, so entsteht neben der beschriebenen kathodischen Stufe ($E_{1/2}$ = —0,375 V) eine weitere kathodische Stufe bei *ca.* $E_{1/2}$ = —0,92 V, die nicht vollständig ausgebildet ist. Ihre Stufenhöhe entspricht etwa der Hälfte der vorher aufgetretenen kathodischen Stufe. Eine weitere schlecht ausgebildete, langgezogene

Stufe entsteht dann im Anschluß daran und bei *ca.* $E_{1/2} = -1{,}74$ V erhält man schließlich eine kathodische Stufe, deren Höhe etwa doppelt so groß ist, wie die der ersten kathodischen Stufe ($E_{1/2} = -0{,}375$ V). Der gesamte Vorgang ist in der Abb. 1 zu sehen.

TABELLE II.—OXYDATION MITTELS WASSERSTOFFPEROXID

3 % H_2O_2 *ml*	Stufe(anod.) *μA*	Stufe(kath.) *μA*	$E_{1/2}$ *V*
0,01	9,7	—	−0,330
0,015	11,1	—	−0,340
0,02	11,3	—	−0,345
0,03	11,5	—	−0,350
0,06	11,3	0,1	−0,355
0,10	11,1	0,5	−0,360
0,15	9,7	1,7	−0,365
0,20	8,5	3,0	−0,370
0,30	6,1	5,0	−0,375
0,40	3,7	7,7	−0,380
0,50	1,1	10,4	−0,375
0,60	—	11,5	−0,380

Temp.: 20°C; Kapillartropfzeit: $t = 3{,}5$ sec; $[Mn^{2+}] = 5{,}45 \,.\, 10^{-3}$ Mol/l.

Volumetrisches Verhalten von Mangan in alkalischer Mannitlösung

Zur Ermittlung des Oxydationsvorganges von zweiwertigen Mangan im gennanten Medium untersuchten wir zunächst die Oxydation mit Kaliumhexacyanoferrat(III). Dabei wurde so verfahren, daß sowohl aus der Lösung, bestehend aus 3 m Kaliumhydroxid und 0,5 m Mannit als auch aus der Mangan(II)-Lösung der Sauerstoff durch Einleiten von Stickstoff restlos entfernt wurde, was nach *ca.* 15 Minuten der Fall war. Danach wurden die beiden Lösungen unter ständigem Einleiten von Stickstoff vereint und das vorhandene Mangan ($1{,}1 \,.\, 10^{-2}$ m) wurde mit einer 0,1 n Kaliumhexacyanoferrat(III)-Lösung potentiometrisch bestimmt. In der Abb. 3 ist der Vorgang veranschaulicht.

Wie aus Abb. 3 ersichtlich, entsprechen die zugefügten Mengen des Hexacyanoferrat(III) den theoretisch berechneten Werten. Während der Titration verfärbt sich die Lösung braun, dann dunkelbraun und schließlich rubinrot und die Potentialwerte stellen sich sofort ein. Der erste Potentialsprung, der der Oxydation von Mangan(II) zu Mangan(III)-Mannit-Komplex entspricht, ist gut ausgeprägt. Der Äquivalenzpunkt liegt bei einem Potentialwert von *ca.* −560 mV, gemessen gegen eine gesättigte Kalomelelektrode. Der zweite Potentialsprung, der der Oxydation vom Mangan(III)-Mannit-Komplex zum Mangan(IV)-Mannit-Komplex entspricht, ist sehr gut ausgebildet. Der Äquivalenzpunkt liegt bei *ca.* −130 mV. Wenn die Lösung vor der Titration mit Sauerstoff oxydiert wird, verschwindet der erste Potentialsprung ($E_{\text{äqu.}} = -560$ mV) und der Verbrauch an Kaliumhexacyanoferrat(III) entspricht der Oxydation von Mangan(III) zu Mangan(IV).

Auf ähnliche Weise wurde die jodometrische Reduktion der genannten Mangan-Mannit-Verbindungen durchgeführt. Dabei wurden 10 ml der alkalischen Mannitlösung mit einem Mangangehalt von $1{,}1 \,.\, 10^{-2}$ m *ca.* eine Stunde mittels Sauerstoff oxydiert. Anschließend wurde die Lösung in eine halbkonzentrierte Salzsäurelösung gegossen, in der überschüssiges Kaliumjodid (*ca.* 1 g) kurz vorher aufgelöst wurde. Das ausgeschiedene Jod wurde sofort mit 0,01 n Natriumthiosulfatlösung titriert. Der Natriumthiosulfat-Verbrauch war grob gesehen äquivalent dem Verbrauch, dwelcher er Reduktion von Mangan(IV) zu Mangan(III) entspricht. Es wurden Blindversuche durchgeführt und die dabei erhaltenen Werte von den erzielten Titrationswerten abgezogen. Die gefundenen Ergebnisse waren stets mit einem negativen Fehler bis zu 10% relativ behaftet.

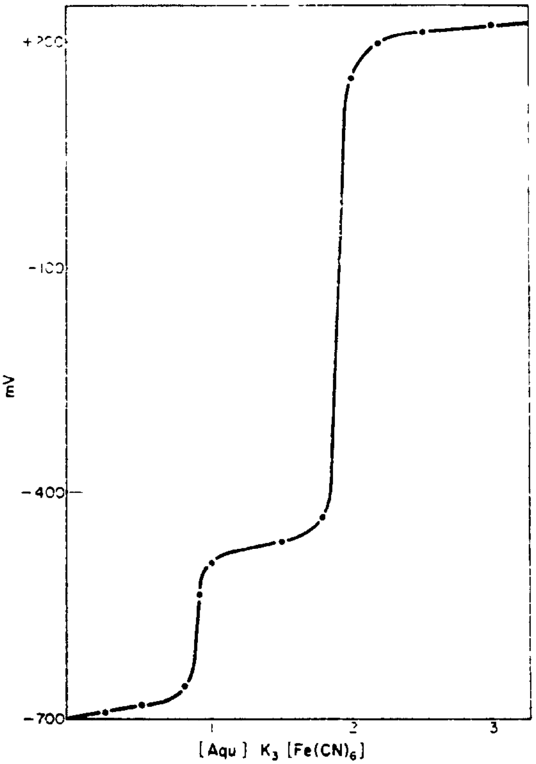

Abb. 3.—Potentiometrische Oxydation von Mangan(II)-Mannit mit $K_3[Fe(CN)_6]$ in alkalischer Lösung.

Spektrophotometrisches Verhalten von Mangan in alkalischer Mannitlösung

Zur weiteren Aufklärung der Wertigkeitsstufen der Mangan–Mannit-Komplexe verwendeten wir die spektrophotometrische Methode. Dabei wurde die vorangegangene Oxydation der Mangan(II)-Lösung polarographisch kontrolliert.

Das Spektrum des braun gefärbten Mangan(III)–Mannit-Komplexes gibt ein gut meßbares Maximum im sichtbaren Bereich bei der Wellenlänge 480 nm und ein kleineres Maximum bei 450 nm. Im UV-Bereich tritt ein kontinuierlicher Anstieg bis zu der Wellenlänge 250 nm auf (siehe Abb. 4 und 5).

Das Spektrum des rubinrot gefärbten Mangan(IV)–Mannit-Komplexes gibt ein gut meßbares Maximum im UV-Bereich bei 285 nm. Im sichtbaren Bereich tritt bereits bei 650 nm ein steiler Absorptionsanstieg in Erscheinung. Bei Anwesenheit

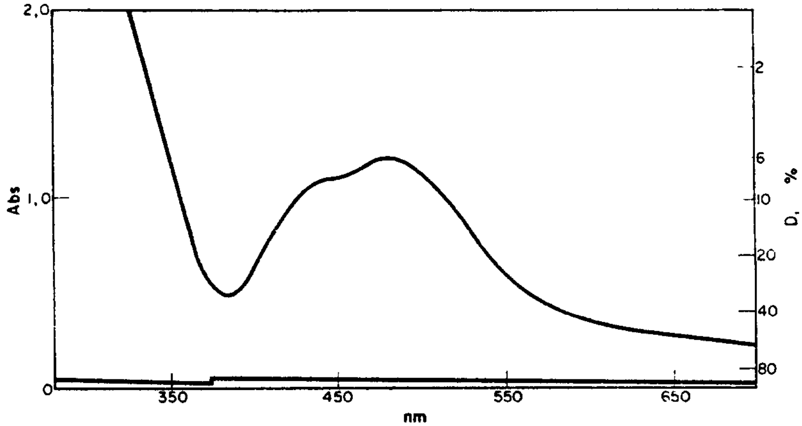

ABB. 4.—Absorptionsspektrum des Mangan(III)-Mannit-Komplexes. Im sichtbaren Bereich: 3 m KOH; 0,5 m Mannit; 5,45 . 10^{-3} m Mn^{++}.

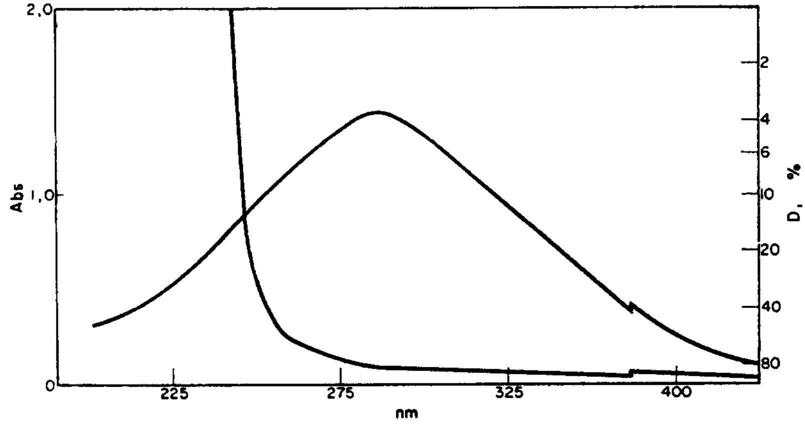

ABB. 5.—Absorptionsspektrum des Mangan(IV)-Mannit-Komplexes. Im UV-Bereich: 3 m KOH; 0,5 m Mannit; 1 . 10^{-4} m Mn^{++}.

des drei- und vierwertigen Mangan–Mannit-Komplexes überdeckt das Absorptionsspektrum des rubinroten vierwertigen Mangan–Mannit-Komplexes das des dreiwertigen Komplexes.

DISKUSSION

Aus den bisher erzielten Ergebnissen kann die Schlußfolgerung gezogen werden, daß das Auftreten der anodischen Mangandoppelstufe bei $E_{1/2} = -0{,}375$ und $E_{1/2} = -0{,}61$ V) auf eine in stark alkalischen Mannit-Lösungen "gehemmte Oxydation" von Mangan(II) am Quecksilbertropfen zurückzuführen ist, die durch das als Niederschlag vorliegende, polarographisch inaktive Mangan(II)-Hydroxid und dessen im Gleichgewicht vorhandenen dissoziierten Mangan(II)-Ionen ausgelöst wird, die mit dem im Überschuß vorhandenen Mannit einen schwachen, polarographisch aktiven Komplex bilden. Die Oxydation dieses Mangan(II)–Mannit-Komplexes erfolgt bei —0,61 V. Aus den Abhängigkeiten der Stufenhöhe von der Wurzel der Reservoirhöhe und Konzentration des Mangans wird ersichtlich, daß der

Elektrodenvorgang nicht durch reine Diffusion ausgelöst wird. Von der Überlegung ausgehend, daß in stark alkalischer Lösung die alkoholischen Hydroxyl-Gruppen größtenteils dissoziiert vorliegen, stellen wir uns folgenden Reaktionsmechanismus vor*

$$\mathrm{Mn(OH)_2} \rightleftarrows \mathrm{Mn^{2+}} + 2\mathrm{OH^-} \tag{I}$$

$$x\mathrm{Mn^{2+}} + y(\mathrm{Mannit} - n\mathrm{H})^{n-} + z\mathrm{OH^-} \rightleftarrows [\mathrm{Mn}_x(\mathrm{Mannit} - n\mathrm{H})_y(\mathrm{OH})_z]^{(2x-ny-z)} \tag{II}$$

$$[\mathrm{Mn}_x(\mathrm{Mannit} - n\mathrm{H})_y(\mathrm{OH})_z]^{(2x-ny-z)} \rightleftarrows [\mathrm{Mn}(\mathrm{Mannit} - n\mathrm{H})_y]^{(2-ny)} + [\mathrm{Mn}_{x-1}(\mathrm{OH})_z]^{(2x-2-z)} \tag{III}$$

Dazu ist zu bemerken, daß die Gleichgewichte der Gleichungen(I) und (II) vom Löslichkeitsprodukt des Mangan(II)-Hydroxids abhängig sind, während die Reaktionsgleichung (III) kinetischen Charakter besitzt. Das bedeutet, daß die Höhe der anodischen Stufe bei $E_{1/2} = -0{,}61$ V durch das Löslichkeitsprodukt des Mangan(II)-Hydroxids gegeben ist. Experimentell konnte nachgewiesen werden, daß diese Stufe kinetischen Charakter besitzt.

Zusammenfassend erhält man die Beziehung (bei $x = 1$ und $z = 2$):

$$\mathrm{Mn(OH)_2} + y(\mathrm{Mannit} - n\mathrm{H})^{n-} \rightleftarrows [\mathrm{Mn}(\mathrm{Mannit} - n\mathrm{H})_y]^{(2-ny)} + 2\mathrm{OH^-} \tag{IV}$$

Demnach wird in stark alkalischer Lösung die Gleichgewichtsverschiebung zum Mangan(II)-Hydroxid begünstigt, wodurch die genannte Oxydationshemmung auftritt und es kann nur der Teil des Mangans oxydiert werden, der als dissoziiertes Ion bzw. als Mangan(II)-Mannit-Komplex in der Lösung vorliegt.

Diese Annahme wird bis zu einem bestimmten Grad durch das Experiment bestätigt, wo wir nachweisen konnten, daß die Höhe der anodischen Stufe bei −0,375 V, die der Oxydation von Mangan(III) zu Mangan(IV) in inerter Atmosphäre entspricht, nur *ca.* 20% der nach der Oxydation mit Sauerstoff erhaltenen anodischen Stufe ausmacht (Tab. I). Wir nehmen weiter an, daß durch die Oxydation das Gleichgewicht der Gleichungen (IV) und (V) zum stabilen braun gefärbten Mangan(III)-Mannit-Komplex verschoben wird:

$$2[\mathrm{Mn}(\mathrm{Mannit} - n\mathrm{H})_y]^{(2-ny)} + \mathrm{H_2O_2} \rightleftarrows 2[\mathrm{Mn}(\mathrm{Mannit} - n\mathrm{H})_y]^{(3-ny)} + 2\mathrm{OH^-} \tag{V}$$

Dieser Oxydationsvorgang verläuft quantitativ nach der theoretisch berechneten Menge, wie bereits beschrieben wurde (Tab. II). Die weitere Oxydation zum Mangan(IV)-Mannit-Komplex erfolgt dann nicht mehr stöchiometrisch nach der Gleichung(VI),

$$\underset{\textit{braun}}{2[\mathrm{Mn}(\mathrm{Mannit} - n\mathrm{H})_y]^{(3-ny)}} + \mathrm{H_2O_2} \rightleftarrows \underset{\textit{rubinrot}}{2[\mathrm{Mn}(\mathrm{Mannit} - n\mathrm{H})_y]^{(4-ny)}} + 2\mathrm{OH^-} \tag{VI}$$

sondern nur durch einen *ca.* 15-fachen Überschuß an Wasserstoffperoxid.

Das Gleichgewicht der Gleichung(VI) wird durch Lichteinwirkung zum dreiwertigen Mangan(III)-Mannit-Komplex verschoben. Diese Photoreduktion ist in

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* $x, y, z = 1, 2, \ldots x, y, z$; $n = 1$ bis 6.

der Abb. 2 veranschaulicht. Wie mit Wasserstoffperoxid werden die gleichen Oxydationseffekte mittels Sauerstoff erzielt.

Unsere ursprüngliche Annahme, daß es sich bei den durch Oxydation erhaltenen drei- und vierwertigen Mangan–Mannit-Komplexen um Peroxo-Verbindungen handelt, konnten wir in keinem Fall bestätigen. Sowohl die jodometrische, als auch die potentiometrische Bestimmung sagt eindeutig aus, daß es sich bei beiden Komplexverbindungen um die genannten Mangan(III)–bzw. Mangan(IV)–Mannit-Komplexe handelt. Bei durchgeführten Blindversuchen, bei denen wir den Proben Wasserstoffperoxid zusetzen, wurden stets viel höhere Manganwerte gefunden, als nach der Theorie berechnet wurde.

Die anodische Stufe bei $E_{1/2} = -0{,}375$ V entspricht demnach der Oxydation vom Mangan(III)– zum Mangan(IV)–Mannit-Komplex. Die kathodische Stufe bei $E_{1/2} = -0{,}375$ V entspricht der Reduktion von Mangan(IV)– zum Mangan(III)–Mannit-Komplex.

Die Ergebnisse der logarithmischen Analyse der beiden polarographischen Stufen zeigen, daß es sich um ein einelektronisches Redox-System handelt, das sich vollständig reversibel verhält. Daß es sich bei beiden Stufen um einen reinen Diffusionsstrom handelt, beweisen die direkt proportionalen Abhängigkeiten der Stufenhöhen von der Wurzel der Reservoirhöhe und der Mangankonzentration. Der bereits diskutierte irreversible Vorgang Mangan(III)–Mannit-Komplex $\rightleftarrows$ Mangan(II)–Mannit-Komplex bzw. Mangan(II)-Hydroxid konnte auch im kathodischen Bereich bestätigt werden. So tritt bei $E_{1/2} = -0{,}92$ V eine Stufe auf, die der Gleichung (V) in rückwärtiger Reaktion entspricht. Die im Anschluß an diese Stufe nach negativen Potentialen zu erhaltene irreversible Stufe kann der Gleichung (IV) bzw. (III → I) zugeschrieben werden. Dabei bremst das an der Quecksilberelektrode gebildete Mangan(II)-Hydroxid die weitere Reduktion, wodurch die zweite, langgezogene Stufe entsteht (*ca.* $E_{1/2} = -1{,}47$ V). Die bei $E_{1/2} = -1{,}74$ V auftretende Stufe entspricht wahrscheinlich der Reduktion Mangan(II) → Mangan(0).

ANALYTISCHE ANWENDUNGEN

Untersuchungen bezüglich des Einflusses der Anionen, Fluorid, Chlorid, Nitrat, Sulfat, Phosphat und Oxalat in einer jeweiligen Konzentration von 0,5 m auf die polarographische Manganbestimmung zeigten, daß diese in mineralischen Rohstoffen sehr häufig anzutreffenden Anionen keine störende Wirkung auf die Manganbestimmung ausüben. Auch die Anwesenheit von 0,5 m ÄDTA und Äthylendiamin in der Probelösung übt auf die Redox-Stufe keinen wesentlichen Einfluß aus. Dieser Effekt ist deshalb von Bedeutung, weil die Halbstufenpotentiale aller Kationen, die mit den genannten Komplexbildnern eine Komplexbildung eingehen nach negativeren Potentialen verschoben werden und dadurch auf die Manganbestimmung keinen störenden Einfluß ausüben. Im praktischen Teil wird dieser Effekt bei der Manganbestimmung eingehend beschrieben. Im angeführten Medium können noch $1 \,.\, 10^{-4}$ m Mangan mit ausreichender Genauigkeit bestimmt werden.

Neben den genannten Anionen wurde auch der Einfluß verschiedener Kationen auf die Manganbestimmung in alkalischer Mannitlösung untersucht. Die erzielten Ergebnisse sind in der Tab. III zu sehen.

Die zweiwertigen Metalle Kupfer, Blei, Zink, Kadmium, die dreiwertigen Antimon, Eisen, Wismut sowie sechswertiges Chrom geben in 3 m Kaliumhydroxid- und 0,5 m

Mannitlösung gut ausgeprägte Reduktionsstufen, die für polarographische Bestimmungen verwendet werden können.

Weiters wurden Manganbestimmungen neben grösseren Konzentrationen an Begleitstoffen durchgeführt. Dabei wurde festgestellt, daß Mangan in Anwesenheit des *ca.* 100-fachen Überschusses an Zink, des *ca.* 80-fachen Überschusses an Chrom, des *ca.* 50-fachen Überschusses an Eisen und Aluminium, sowie des *ca.* 20-fachen Überschusses an Kupfer und Nickel noch gut reproduzierbare polarographische Stufen liefert. Bei noch größeren Beimengungen des Mangans muß die Methode der Standardzugabe angewendet werden.

TABELLE III.—DER EINFLUß VERSCHIEDENER KATIONEN

Kation	*V*	$E_{1/2}$ gegen SCE, Bemerkung
Co^{2+}	(1) −0,30 (2) −1,51	(1) anodische Stufe (2) kath Stufe
As^{3+}	−0,30	anodische Stufe
$Mn^{3+/4+}$	−0,37	revers anodische-kathodische Stufe
Tl^{+}	−0,48	rev. kath. Stufe
Cu^{++}	−0,57	rev. kath. Stufe
Bi^{3+}	−0,76	rev. kath. Stufe
$CrO_4{}^{2-}$	−0,82	rev. kath. Stufe
Pb^{2+}	−0,84	rev. kath. Stufe
Cd^{2+}	−0,85	rev. kath. Stufe
Sb^{3+}	(1) −0,43 (2) −1,22	(1) anodische Stufe, (2) kathodische Stufe
Fe^{3+}	(1) −1,15 (2) −1,65	(1) kath. Stufe (2) kath. Stufe
Fe^{2+}	(−1,22)	irreversible Stufe
Sn^{2}, Ni^{2+}, Cr^{3+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}	keine Stufen	

T = 20°C; Kapillartropfzeit $t = 3$ sek; Eingesetzte Kationenkonz.: $5 \,.\, 10^{-3}$ Mol/l. Elektrolytlösung: 3 m KOH und 0,5 m Mannit.

Die Manganbestimmung wird in Gegenwart von zweiwertigem Kobalt gestört, das im genannten Medium an der Quecksilbertropfelektrode eine schlecht ausgeprägte anodische Stufe mit dem Halbstufenpotential von *ca.* −0,30 V bildet. Nach Oxydation des vermutlich zweiwertigen Kobalt–Mannit-Komplexes mit Sauerstoff, entsteht eine langgezogene anodisch–kathodische Stufe bei *ca.* −0,30 V. Die Reduktion des zweiwertigen Kobalts erfolgt bei $E_{1/2} = -1{,}51$ V. Den störenden Einfluß von Kobalt auf die Manganbestimmung konnten wir durch Zugabe von Äthylendiamin zur Probelösung eliminieren. Wie aus der Arbeit von Doležal und Nowak[7] hervorgeht, bildet Kobalt in einer Lösung von 1 m Kaliumhydroxid und 1 m Äthylendiamin einen sehr stabilen Komplex, dessen Reduktion an der Quecksilbertropfelektrode bei $E_{1/2} = -0{,}71$ V (SCE) erfolgt.

In einer Lösung von 3 m Kaliumhydroxid, 0,5 m Mannit und 0,5 m Äthylendiamin wird zweiwertiges Kobalt durch Einleiten von Sauerstoff nach *ca.* 20 sec (die Oxydation erfolgt auch leicht mit Luft) quantitativ zum dreiwertigen Kobalt-Komplex oxydiert. Der Komplex bildet eine kathodische Stufe bei −0,84 V und übt damit auf die Manganbestimmung keinen störenden Einfluß mehr aus. Die Oxydation des zweiwertigen Kobalts ist notwendig, da sich sonst trotz des anwesenden Äthylendiamins eine störende anodische Stufe bei −0,45 V bildet. Im genannten Medium wird weder die Stufenhöhe noch das Halbstufenpotential der Mangan-Redox-Welle verändert, daher können noch 1 . 10^{-4} m Mangan bestimmt werden. Außerdem kann Mangan in Gegenwart von Kobalt noch in einem Konzentrationsverhaltnis von 1:20 mit guter Genauigkeit bestimmt werden. Einen Überblick über weitere Möglichkeiten der polarographischen Manganbestimmung zeigt die Tabelle IV, in der die von uns gefundenen Werte im genannten Medium wiedergegeben sind.

TABELLE IV.—DER EINFLUß VERSCHIEDENER KATIONEN IN GEGENWART VON ÄTHYLENDIAMIN

Kation	Gef. $E_{1/2}$ gegen SCE, V	Bemerkung
Sb^{3+}	−0,23	irrev. anod. Stufe
As^{3+}	−0,31	irrev. anod. Stufe
$Mn^{3+/4+}$	−0,38	rev. anodisch-kathodische Stufe
Co^{2+}	−0,45	(in inerter Atmosphare) anod. Stufe
Tl^{+}	−0,49	rev. kath. Stufe
Cu^{2+}	−0,66	rev. kath. Stufe
Co^{3+}	−0,84	rev. kath. Stufe
Cd^{2+}	−1,01	rev. kath. Stufe
Pb^{2+}	−1,03	rev. kath. Stufe
Bi^{3+}	−1,05	rev. kath. Stufe
CrO_4^{2-}	−1,11	rev kath. Stufe
$Fe^{3+/2+}$	−1,23	kath. Stufe (langgezogen)
Sb^{5+}	−1,38	kath. Stufe (langgezogen)
Ni^{2+}	−1,39	kath. Stufe (langgezogen)
Zn^{2+}	−1,62	rev. kath. Stufe
Cr^{3+}, Al^{3+},	keine Stufen	—
Mg^{2+}, Ca^{2+},		—
Sr^{2+}, Ba^{2+}		—

T = 20°C; Kapillartropfzeit t = 3 sek; Eingesetzte Kationenkonz.: 5 . 10^{-3} Mol/l. Elektrolytlösung: 3 m KOH + 0,5 m Mannit + 0,5 m Äthylendiamin.

PRAKTISCHE METHODEN

Polarographische Bestimmung von Mangan im Dolomit-Gestein

Es wurden *ca.* 2 g der fein verriebenen Probe mit 20 ml Salzsäure (1:4) im Becherglas aufgelost, die Lösung eingedampft, erneut mit etwas Salzsaure versetzt und mit 50 ml bidest. Wasser verdünnt. (Da nur wenig Kieselsäure vorhanden war, wurde diese mit in ein 100-ml Maßkolbchen überführt.) Zur sauren Lösung wurde tropfenweise 12 m Kaliumhydroxidlösung bis zur schwach alkalischen Reaktion zugegeben und mit bidest. Wasser auf 100 ml aufgefullt. Von dieser Lösung wurden je 1 ml in zwei 10-ml Maßkolbchen abpipettiert, dazu je 2,5 ml 12 m Kaliumhydroxid-, 2,5 ml 20%ige Mannit- und 2,5 ml 2 m Äthylendiamin-Lösung und in eines der beiden noch 0,5 ml Standardlosung

((1 ml = 2,75 mg Mn) gegeben und mit bidest. Wasser aufgefüllt. Von beiden Lösungen wurden je 5 ml in ein Kalousek-Gefäß abpipettiert, 1 Minute Sauerstoff, 5 Minuten Stickstoff durchgeleitet und die polarographische Bestimmung gegen eine gesättigte Kalomelelektrode durchgeführt. Es wurde mit einer Empfindlichkeit von 1:20 gemessen. Die Ergebnisse sind gut reproduzierbar und mit einem relativen Fehler von ±2% behaftet.

TABELLE V.

Probe	Mangan, %	
	Polarog.	Gravim.
Dolomit 1	2,29	2,34
Dolomit 2	2,31	2,32
Schiefer 1	1,32	1,35
Schiefer 2	1,28	1,32

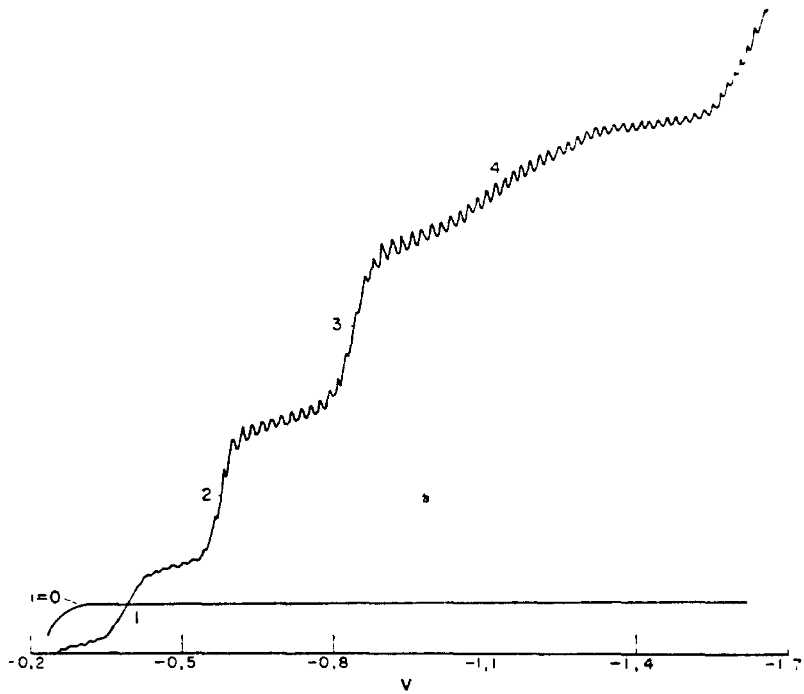

ABB. 6.—Polarographische Manganbestimmung neben Kupfer Blei und Eisen. Konz. der Elektrolytlsg.: 3 m KOH; 0,5 m Mannit. Konz. der eingesetzten Kationen: (1) $1 . 10^{-3}$ m Mn^{2+} (2) $1 . 10^{-3}$ m Cu^{2+}; (3) $1 . 10^{-3}$ m Pb^{2+}, (4) $2 . 10^{-3}$ m Fe^{3+}. Empfindlichkeit: 15 μA.

Polarographische Bestimmung von Mangan im Schiefer

Es wurde 1 g der fein verriebenen Probe im Platintiegel mit der *ca.* sechsfachen Menge eines Natriumcarbonat/Kaliumcarbonat-Gemisches aufgeschlossen. Nach dem Abkühlen wurde der Tiegel im Becherglas mit dest. Wasser ausgelaugt, zur Lösung 5 ml konz. Salzsäure zugefügt und zur Trockne eingedampft. Nach dem Abkühlen wurde der Rückstand mit halbkonz. Salzsäure aufgelöst und erneut zur Trockne eingedampft (Wasserbad). Der Rückstand wurde mit 10 ml konz. Salzsäure aufgenommen und mit 50 ml Wasser verdünnt. Die ausgeschiedene Kieselsäure wurde abfiltriert und 2 mal mit 10 ml heissen Wasser gewaschen. Das Filtrat im 100-ml Kolben wurde mit

12 m Kaliumhydroxid neutralisiert und mit bidest. Wasser aufgefüllt. Von dieser Lösung wurden je 2 ml in zwei 10-ml Maßkölbchen abpipettiert, je 2,5 ml 12 m Kaliumhydroxid, 2,5 ml 0,2 m ÄDTA—und 2,5 ml 20%ige Mannitlosung zugefügt. Zu der einen Lösung wurden ausserdem noch 0,25 ml Standardlosung (1 ml = 2,75 mg Mn) zugegeben.

Die beiden Maßkölbchen wurden zur Marke aufgefüllt, davon je 5 ml in ein Kalousek-Gefäss überführt und die polarographische Bestimmung in beschriebener Weise durchgeführt. Die Ergebnisse sind gut reproduzierbar, der relative Fehler betrug ±2%. Siehe Tab. V.

Polarographische Bestimmung von Mangan neben Kupfer, Blei und Eisen

Eine Lösung von 5 bis 10 ml mit den genannten Kationen muß auf einen Mannitgehalt von 0,5 m und auf einen Kaliumhydroxid-Gehalt von *ca* 3 m gebracht werden. Anschließend wird in die Lösung Sauerstoff (*ca.* 1 min) und Stickstoff (*ca.* 5 min) eingeleitet und 3 Tropfen 0,5%ige Gelatine zugefügt. Die Mangankonzentration soll mindestens 1 . 10^{-4} m betragen. Der Gehalt der Lösung an Kupfer, Blei und Eisen darf die bereits angeführten Konzentrationsverhältnisse zum Mangan nicht überschreiten. Zur Veranschaulichung der im angegebenen Medium gut reproduzierbaren polarographischen Stufen dient das in der Abb. 6 wiedergegebene Polarogramm.

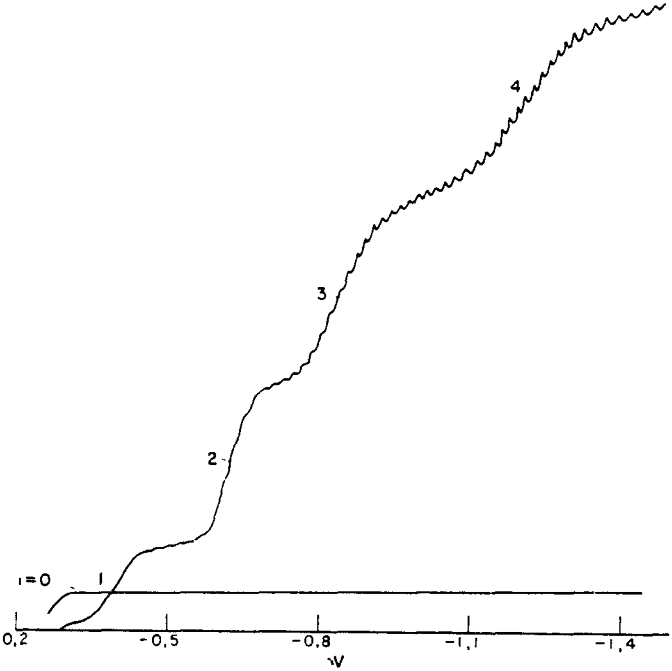

Abb. 7.—Polarographische Manganbestimmung neben Kupfer, Kobalt und Eisen. Konz. d. Elektrolytlsg.. 3 m KOH; 0,5 m Mannit und 0,5 m Äthylendiamin. Konz. der eingesetzten Kationen. (1) 1 . 10^{-3} m Mn^{2+}, (2) 1 . 10^{-3} m Cu^{2+}, (3) 2 . 10^{-3} m Co^{2+}, (4) 2 . 10^{-3} m Fe^{3+}. Empfindlichkeit: 15 μA.

Polarographische Bestimmung von Mangan neben Kobalt, Kupfer und Eisen

Die zur polarographischen Manganbestimmung vorliegende Lösung muß einen Gehalt von 3 m Kaliumhydroxid, 0,5 m Mannit und 0,5 m Äthylendiamin aufweisen. Die Mangankonzentration soll mindestens 1 . 10^{-4} m betragen, Kobalt und Kupfer können *ca.* das 20-fache der Mangankonzentration in der Lösung ausmachen, wenn keine weiteren Stoffe vorliegen. Andernfalls kann die Anwesenheit weiterer Stoffe einen Konzentrationsniederschlag in der Lösung herbeiführen, der die Manganbestimmung stört. Die Bestimmung (wie auch die vorher genannten) muß den jeweiligen Versuchsbedingungen angepaßt werden. Eventuell muß das im großen Überschuß vorliegende Kation abgetrennt werden. Zur Veranschaulichung der gut reproduzierbaren Stufen ist das Polarogramm in der Abb. 7 wiedergegeben.

Summary—The formation of manganese-mannitol complexes in alkaline solution has been studied polarographically, and it has been shown that manganese(II) hydroxide is oxidized by oxygen or hydrogen peroxide to the brown manganese(III)-mannitol complex and then to the red manganese(IV)-mannitol complex. At the dropping mercury electrode, the manganese(III)-mannitol → manganese(IV)-mannitol system is reversible, with $E_{1/2} = -0{\cdot}375$ V. The probable reaction mechanism is discussed. Manganese may be determined polarographically in the presence of a 20-fold excess of copper in a solution $3M$ in potassium hydroxide and 0 $5M$ in mannitol, at concentrations down to $10^{-4}M$. When the solution also contains ethylenediamine (0 $5M$), interferences from cobalt and iron(III) are removed. The $E_{1/2}$ values for 21 cations in this electrolyte are reported. The method has been applied to the determination of manganese in dolomites and slates.

Résumé—On a étudié polarographiquement la formation des complexes de manganèse avec mannitol dans un milieu alcalin, et on a etabli que l'hydroxide de manganèse(II) est oxydisé par oxygène ou peroxyde d'hydrogène au complexe brun manganèse(III)-mannitol, donc au complexe rouge manganèse(IV)-mannitol Le système manganèse(III)-mannitol → manganèse(IV)-mannitol est polarographiquement reversible; $E_{1/2} = -0{,}375$ V. On discute la course probable de réaction On peut doser polarographiquement le manganèse en présence d'une quantité 20 fois supérieure de cuivre dans une solution $3M$ en potasse et $0{,}5M$ en mannitol, à des concentrations pouvant descendre jusqu'à $10^{-4}M$. Lorsque la solution contient aussi de l'éthylènediamine ($0{,}5M$), les interférences dues au cobalt et au fer(III) sont éliminées. On donne les valeurs de $E_{1/2}$ pour 21 cations dans cet électrolyte. On a appliqué la méthode au dosage du manganèse dans les dolomites et ardoises.

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EXTRACTION OF TITANIUM(IV) GALLATE INTO TRI-ISO-OCTYLAMINE AND ITS SPECTROPHOTOMETRIC DETERMINATION

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Summary—Extraction of titanium(IV) gallate species into tri-iso-octylamine (TIOA) has been studied to develop a spectrophotometric method for the determination of titanium. The behaviour of common ions, under the conditions for quantitative extraction of titanium, is reported. Examples are given of application of the method to analysis of steels, reactor-grade thoria, and silicate rocks.

IN THE spectrophotometric determination of titanium with gallic acid,[1] interference due to a few other ions is reported.[2] It has been observed in this laboratory that tri-iso-octylamine (TIOA) extracts a coloured species from the titanium(IV)–gallic acid system.[3] With a view to developing a sensitive and selective method, the extraction of the titanium gallate species into TIOA has been investigated.

EXPERIMENTAL

Reagents

TIOA solution. Colourless "practical grade" reagent was dissolved in toluene to give an approx. 0·1*M* solution, which was standardized with standard perchloric acid in glacial acetic acid.[4] The standardized amine solution was equilibrated with ~2*N* sulphuric acid, washed with distilled water till free from acid, filtered through a dry filter paper and stored in an amber bottle.

Titanium solution. A known weight of ignited Merck "Extra Pure" grade titanium dioxide was dissolved in hydrofluoric acid, and 25 ml of sulphuric acid (1 + 1) were added. The solution was evaporated and fumed to remove the fluoride, cooled, and diluted to 250 ml with cold water.

Gallic acid. Merck "Extra Pure" grade reagent was crystallized twice from hot water and carefully dried at 120°. Fresh solutions were prepared as and when required.

All other reagents were of analytical grade.

Development of method

The effect of pH and the concentration of gallic acid and TIOA on the absorbance (*A*) of the extracted titanium was studied by equilibrating the amine solution with an equal volume of aqueous medium under different conditions and measuring the absorbance of the organic phase at 390 mμ against a corresponding blank (amine solution) equilibrated with aqueous medium containing all reagents except titanium. The results are recorded in Table I. After equilibration the aqueous phase was always tested for its titanium content. When the pH of the aqueous phase was raised above 2·5, some yellow solid appeared at the interface.

In all these experiments, no titanium was detected in the aqueous phase after equilibration with amine, indicating practically quantitative extraction of titanium in a single equilibration. However, the absorbance of the extracted titanium species was greatest when the pH was between 1·5 and 2·5 and the concentrations of gallic acid and TIOA were 0·04*M* and 0·020–0·026*M* respectively. The variation of absorbance of the organic phase for the same quantity of titanium shows the existence of more than one coloured species in the organic phase. Since an increase or decrease of TIOA from the range 0·020–0·026*M* causes a decrease in the absorbance, the effect of gallic acid on the degree of extraction of titanium and on the absorbance was studied at two more concentrations of TIOA and the results are given in Table II. The titanium remaining in the aqueous phase after equilibration with the amine was determined spectrophotometrically.[5]

TABLE I.—ABSORBANCE OF EXTRACTED TITANIUM

No.	pH	Gallic acid, *M*	TIOA, *M*	TiO$_2$ taken, μg	A_{390}
Variation of pH					
1	0·6	0·04	0·105	23·0	0·380
2	0·7				0·430
3	0·9				0·445
4	1·3				0·460
5	1·5				0·470
6	1·7				0·470
7	2·0				0·465
8	2·2				0·470
9	2·5				0·470
Variation of gallic acid concentration					
10	1·8	0·01	0·105	23·0	0·365
11		0·02			0·420
12		0·03			0·450
13		0·04			0·470
14		0·05			0·465
Variation of TIOA *concentration*					
15	1·8	0·04	0·15	16·0	0·315
16			0·105		0·325
17			0·053		0·330
18			0·042		0·335
19			0·026		0·348
20			0·021		0·345
21			0·015		0·300
22			0·0105		0·265

TABLE II.—EFFECT OF GALLIC ACID ON THE EXTRACTION OF TITANIUM

TIOA, *M*	Gallic acid, *M*	A_{390}	Extraction, %
0·0105	0·005	0·080	25
	0·01	0·290	62·5
	0·02	0·410	81
	0·03	0·460	91
	0·04	0·465	100
	0·05	0·508	100
0·021	0·02	0·590	100
	0·03	0·665	100
	0·04	0·690	100
	0·045	0·700	100
	0·05	0·690	100

TiO$_2$ 32 μg; pH 1·7.

The results in Table II show that the extraction of titanium with 0·0105*M* TIOA is quantitative only when the gallic acid concentration is 0·04*M* or above, while with 0·021*M* TIOA it is quantitative even with 0·02*M* gallic acid. However, the absorbance of the titanium species is greatest when the TIOA concentration is 0·021*M*. It is not practicable to increase the gallic acid concentration above 0·05*M*, owing to its low solubility.

By use of 0·021*M* TIOA and 0·04*M* gallic acid, the effect of pH on the absorbance of the extracted titanium was studied again and found to be similar to that in experiments 1–9 in Table I. Under these conditions the spectrum of the titanium in the amine phase was recorded. It exhibits a broad peak with a maximum at 390 mμ. By the procedure given below, a calibration curve was obtained for titanium in the range 4–32 μg of TiO$_2$ per 10 ml of organic phase and found to be linear; the molar absorptivity of 17·2 × 10^3.

Procedure

Take an aliquot of sample containing 10–80 μg of titanium dioxide, add to it 10 ml of 0·1*M* gallic acid and 2 ml of 1% ascorbic acid to prevent interference by iron(III), adjust the pH to 2·0 ± 0·1 with ~1*M* sodium acetate and dilute to 25 ml in a standard flask. Take 10 or 20 ml of this solution (according to titanium content) and equilibrate in a separating funnel with an equal volume of 0·02*M* amine sulphate solution for 3 min. Allow the layers to separate. Filter the organic phase through a dry filter paper into the absorption cell and measure the absorbance at 390 mμ against amine sulphate solution equilibrated with a reagent blank.

Interferences

The behaviour of some cations and anions was studied under these experimental conditions. The results are noted in Table III. Iron(II), copper(II), nickel, chromium(III), manganese(II) and cobalt(II) ions show no extraction and as such do not interfere. Iron(III), vanadate, molybdate and tungstate ions are partly extracted and also impart colour to the amine phase. The interference of vanadate is minimized by addition of ascorbic acid.

Since sulphate and acetate are used in the procedure, their effect was studied by analysing synthetic mixtures. The results are given in Table IV.

TABLE III.—BEHAVIOUR OF SOME COMMON IONS

Ion	Amount, *mg*	Ascorbic acid, added, *mg*	A_{390}	Distribution ratio
Fe(III)	0·056	—	0·104	0·1
	0·056	20	0·002	—
	20	20	0·305	—
	20	40	0·180	—
	20	60	0·005	—
	20	80	0·003	—
	20	100	0·002	—
Cu(II)	0·080	—	0·001	0
Ni(II)	0·085	—	0·000	0
Cr(III)	0·200	—	0·000	0
Mn(II)	0·120	—	0·000	0
Co(II)	0·100	—	0·002	0
V(V)	0·224	—	0·020	2·2
	0·224	20	0·004	1·9
Mo(VI)	0·040	—	0·265	40
	0·040	20	0·270	40
W(VI)	0·400	—	0·140	4
Th(IV)	90	—	0·005	0·002
Al(III)	15	—	0·000	0
Be(II)	15	—	0·000	0
UO_2(II)	0·200	—	0·000	10*

The element left in the aqueous phase after equilibration was determined by standard colorimetric methods[5] after destruction of the organic matter.

* Probably extracted as sulphate complex.

TABLE IV.—EFFECT OF SULPHATE AND ACETATE

Salt	Amount, *mg*	TiO_2 found, μg	Error, μg
Potassium sulphate	100	32·0	0·0
	300	32·2	+0·2
	500	31·6	−0·4
Sodium acetate	34	32·0	0·0
	68	31·8	−0·2
	136	32·0	0·0

TiO_2 taken—32·0 μg.

APPLICATIONS

Stabilized steels

In some of the methods for the determination of titanium in steels,[5–7] chromium, nickel, cobalt, *etc.* interfere. In others[8–13] the separation of titanium from other elements is time-consuming. The method described here is applicable to steels with advantage.

The results in Table III show that 80 mg of ascorbic acid will reduce the interference of 20 mg of iron(III) to a tolerable level. Because ascorbic acid forms coloured complexes with titanium(IV),[14] the effect of 60–100 mg of it on the titanium determination was studied, along with the effect of 8–12 mg of chromium(III), 20–25 mg of nickel and 10–15 mg of cobalt(II). The maximum deviation in the determination of 8·0 μg of titanium dioxide was ±0·2 μg. Interference from molybdenum and tungsten can be eliminated by hydroxide precipitation, filtration, and dissolution of the precipitate in sulphuric acid to yield the solution for titanium extraction. Typical results are shown in Table V (samples 5 & 6).

Procedure. Dissolve 0·1–0·5 g of the steel in 25 ml of hydrochloric acid and a little nitric acid in a beaker. Add 10 ml of sulphuric acid (1 + 1) and evaporate the solution till fuming. Cool and dilute to 50 ml, boil, and filter through Whatman No. 40 filter paper. Ignite the residue, treat it with hydrofluoric and sulphuric acids and ignite it again. Fuse this residue with potassium bisulphate, cool, dissolve the melt in 5% sulphuric acid, add to the main solution and dilute this to 100 ml, the final acidity being equivalent to 5% sulphuric acid.

To an aliquot of the same solution, add 10 ml of 0·1*M* gallic acid and an amount of ascorbic acid equal to five times the weight of the sample in the aliquot. Adjust the pH to 2·0 ± 0·1 with 1*M* sodium acetate and dilute to 25 ml in a standard flask. Transfer 10 or 20 ml of this solution into a separating funnel and equilibrate it with an equal volume of 0·020–0·026*M* amine sulphate in toluene for 3 min. Separate the phases, filter the amine layer through a dry Whatman No. 40 filter paper, and measure its absorbance at 390 mμ against amine sulphate equilibrated with the reagent blank. Prepare a calibration curve with standards treated similarly.

TABLE V.—ANALYSIS OF STANDARD STEEL SAMPLES

Sample	Ti expected, %	Ti obtained, %
1. B.C.S. No. 235/1 (Stabilized stainless steel)	0·36	0·37 0·37
2. B.C.S. No. 233 (Permanent magnet alloy)	0·79	0·79 0·80
3. B.C.S. No. 236/1 (Haematite iron)	0·065	0·068 0·063
4. B.C.S. No. 206 (Cast iron)	0·16	0·17 0·17
5. B.C.S. No. 220 (H.S. steel)	1·60	1·60
6. B.C.S. No. 241 (H.S. steel)	1·60	1·55

Samples 1 to 4 contain <0·04% Mo and W. Sample 5 contains 6·74% W and 4·17% Mo, and sample 6 contains 20·28% W and 0·54% Mo; a known amount of titanium was added to both these samples.

Reactor-grade thoria

Hydrogen peroxide,[15,16] oxine[17,18] and tiron[15] have been used to determine titanium in the presence of thorium but their sensitivities are too low for application to reactor-grade thoria containing less than 50 ppm of titanium.

Synthetic samples containing thorium sulphate and known amounts of titanium were analysed by the present method and the results are given in Table VI along with those for some sintered thoria samples from Atomic Fuels Division, BARC. The standard addition technique was used to assess the accuracy of the method.

Procedure. Weigh accurately 0·1 g of the thoria powder and dissolve it in 20 ml of nitric acid and 2 or 3 drops of 2% hydrofluoric acid. Evaporate to dryness on a water-bath. Add 5 ml of 5% sulphuric acid and heat to copious fuming. Cool, and dissolve the residue in a few ml of water. Add enough gallic acid to give a final concentration of 0·04*M*, and adjust the pH to 2·0 with sodium acetate. Dilute to about 15 ml, and extract the titanium with 10 ml of amine sulphate solution.

TABLE VI.—DETERMINATION OF TITANIUM IN SYNTHETIC AND SINTERED THORIA SAMPLES (100-mg SAMPLES)

No.	TiO_2 added, μg	TiO_2 found, μg
1	—	0·2
2	8·0	7·8
3	16·0	16·2
4	—	2·1
	2·0	4·0
5	—	1·7$_5$
	2·0	3·8$_5$
6	—	1·4$_5$
	2·0	3·3$_5$

1, 2 and 3 are thorium nitrate samples from Indian Rare Earths Ltd., Bombay. 4, 5 and 6 are sintered thoria samples from Atomic Fuels Division of this Centre.

Silicate rocks

Various methods have been reported for the determination of titanium in silicate rocks.[19–24] They have their own advantages and disadvantages, but in view of the selectivity and sensitivity of the present method, its extension to this problem was studied. Typical results are given in Table VII.

Procedure. Fuse 0·5 g of sample with 5 g of sodium carbonate in a platinum crucible for 1 hr (test first for presence of the acid sulphide group). Dissolve the cooled melt in hydrochloric acid, evaporate the solution to dryness and bake. Treat the dry mass with dilute hydrochloric acid and filter. Ignite the residue, treat it with hydrofluoric and sulphuric acids, ignite it again, and fuse the residue with potassium bisulphate. Dissolve the cooled melt in dilute acid and add it to the main solution. Add ammonium chloride and ammonia solution, filter off the hydroxides, wash them and dissolve them in 5% sulphuric acid. Dilute the solution to 100 ml. Add 20 mg of ascorbic acid to a suitable aliquot and extract as described under the procedure for steels. An alternative is to use the Berzelius method for removal of silica and bringing the sample into solution.

TABLE VII.—ANALYSIS OF SILICATE SAMPLES FOR TiO_2

TiO_2 by peroxide method,[19] %	TiO_2 by present method, %
0·51	0·53
0·80	0·78
0·50	0·52
1·00	0·96
2·00	1·97

CONCLUSION

The method described is far more sensitive than the widely used peroxide method but less sensitive than some others.[2,7,25–27] In selectivity it compares well with the thiocyanate–TOPO method,[26] while other more sensitive methods are less selective.

In view of its good selectivity and sensitivity, it can be applied to some specific problems with advantage.

Résumé—On a étudié l'extraction de l'espèce gallate de titane(IV) en tri isooctylamine (TIOA) pour élaborer une méthode spectrophotométrique de dosage du titane. On décrit le comportement d'ions communs dans les conditions d'extraction quantitative du titane. On donne des exemples d'application de la méthode à l'analyse d'aciers, de thorine qualité réacteur et de roches au silicate.

Zusammenfassung—Zur Entwicklung einer spektrophotometrischen Methode zur Bestimmung von Titan wurde die Extraktion von Titan(IV)-Gallat-Spezies in Triisooctylamin (TIOA) untersucht. Es wird über das Verhalten haufig vorkommender Ionen unter den Bedingungen der quantitativen Titanextraktion berichtet. Beispiele der Anwendung der Methode auf die Analyse von Stahlen, von reaktorreinem Thoriumdioxid und von Silikatgesteinen werden angegeben.

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CALMAGITE AS A SPECTROPHOTOMETRIC REAGENT FOR ALUMINIUM

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Summary—Calmagite is proposed as a sensitive spectrophotometric reagent for aluminium, $\varepsilon_{570m\mu} = 42000$. After aqueous phase reaction at pH 8 6, the metal–reagent complex is extracted into chloroform by formation of an ion-association complex with a quaternary ammonium salt. The method is free from interference by common anions, and cationic interferences may be eliminated by the use of cyanide and EDTA as masking agents.

NUMEROUS spectrophotometric methods for the determination of aluminium have been published.[1] The most frequently used reagent is probably aluminon, but, more recently, more sensitive reagents *e.g.*, stilbazo ($\varepsilon = 34600$), Eriochrome Cyanine R ($\varepsilon = 57000$) and Chrome Azurol S ($\varepsilon \sim 50000$) have been widely applied. Almost all methods are carried out in the pH range 3–7 and are subject to many interferences.

In the present study, the metallochromic properties of a number of *o,o'*-dihydroxyazo dyes were investigated both in aqueous solution and after extraction into chloroform as ion-association complexes. Several potentially applicable reactions were noted. This communication describes the work which has been carried out to characterize the aluminium–Calmagite system.

Calmagite, 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulphonic acid, was first introduced by Lindstrom and Diehl[2] as a stable replacement for Eriochrome Black T in the EDTA titration of calcium and magnesium. Its behaviour is summarized in Diehl's monograph.[3]

After aqueous phase reaction between the metal and Calmagite at pH 8·6, the negatively-charged complex is extracted into chloroform by association with a quaternary ammonium salt. Methyltricaprylylammonium chloride is used as the extracting agent but several other tertiary ammonium salts are equally suitable. Many interferences may be eliminated by the use of cyanide and EDTA as masking agents.

EXPERIMENTAL

Apparatus

Samples were prepared in 45-ml cylindrical tubes, fitted with polyethylene stoppers and plastic screw-caps. These were shaken in an Eberbach Reciprocating Shaker at the high-speed setting. Water at 25·0 ± 0 2° from a Wilkens-Anderson Co. Lo-Temp. bath was circulated through the jacketed shaker tray.

Absorption spectra and quantitative spectrophotometric measurements were obtained with a Beckman DB spectrophotometer. A Beckman Model G pH meter with a glass-calomel electrode pair

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was calibrated with Beckman buffer solutions at pH 7·00 and 10·00, and used for all pH measurements.

Reagents

Buffer pH 8·6. Volumes of 450 ml of 0·1*M* boric acid (AR grade, Mallinckrodt) and 250 ml of 0·1*M* sodium tetraborate (AR grade, Mallinckrodt) were mixed and diluted to 2 l. with distilled water. Anhydrous sodium perchlorate (39·4 g, G. F. Smith Chemical Co.) was added to make the ionic strength of the stock buffer solution 0·3.

Calmagite. A 0·15-g amount of Calmagite (City Chemical Corp.) was dissolved in 1 litre of distilled water. The slight turbidity which persisted even after prolonged stirring was removed by filtration. This solution was used for all the work on the development of the analytical procedure. The purity of this reagent was checked by measuring the molar absorptivity of solutions at pH 10·0 and 610 mμ.[3] These experiments indicated a purity of 47% if it was assumed that none of the impurities present absorbed at this wavelength. The stock reagent solution used was therefore approximately 1·94 × $10^{-4}M$.

The purity of another sample of Calmagite (K and K Labs.) was found to be approx. 60% and solutions prepared from "corrected" weights of this sample were used for the experiments to determine the nature of the complex. It was noted that both batches of Calmagite had a strong phenolic odour, probably indicating the presence of *p*-cresol, one of the starting materials in the synthesis of Calmagite.

Methyltricaprylylammonium chloride. This reagent was obtained as Aliquat 336 (General Mills, Chemical Division, Kankakee, Illinois). No attempt was made at purification. An approximately 0·1*M* solution was prepared by dissolving 40 g in 1 litre of chloroform (AR grade, Mallinckrodt).

Aluminium and other metal ion solutions were prepared from their perchlorates (G. F. Smith Chemical Co.). Anionic interferences were investigated by using the sodium salts (generally analytical grade).

Spectral characteristics

Figure 1 shows the absorption spectra of Calmagite and its aluminium complex after extraction with a chloroform solution of Aliquat 336 from aqueous solution at pH 8·7. Under these conditions the aluminium complex is purple and the reagent blank is orange. The optimum wavelength for measurement of the aluminium complex is 570 mμ.

Establishment of optimum conditions for aluminium determination

The factors affecting the system and its potential as a spectrophotometric procedure were investigated in a standard manner.[4] During the preliminary qualitative investigations, the extractable purple aluminium-Calmagite complex was observed to form above *ca.* pH 8. The absorbance of this complex was maximal over the range pH 8·2–8·8. The optimum pH region for the analytical determination is 8·6–8·7. Since the p*K* for the dissociation of Calmagite, $H_2D^- \rightleftharpoons HD^{2-} + H^+$, is 8·14,[2] at pH 8·6 approx. 75% of the dye is present in the form HD^{2-}.

It was shown that a five-fold molar excess of reagent over aluminium was sufficient to develop fully the colour of the complex and that a further increase in the reagent concentration had no effect on the absorbance due to a given amount of aluminium. A ten-fold molar excess of Calmagite was used in the analytical work. It was also shown that a nominal 3000-fold molar excess of Aliquat 336 over aluminium was necessary to ensure total extraction of the metal complex and this concentration was used.

The aluminium–Calmagite complex is not formed instantaneously at pH 8·6 and 30 min should be allowed after mixing of the aluminium, reagent and buffer solutions for the aqueous phase complexation to proceed to completion. After addition of the chloroform solution of Aliquat 336, a shaking time of 2 min is adequate to ensure total extraction of the ion-association complex. The absorbance of the extract is then constant for several hr and is conveniently measured after 30–60 min.

Procedure

To 5 ml of pH 8·6 buffer in a shaking-tube, add 4 ml of 4 × $10^{-4}M$ Calmagite, appropriate volumes up to 5 ml of solution containing 1·1–5·4 μg of aluminium, and distilled water as necessary to make the volumes equal. Mix well and allow to stand for 30 min. Now add 10 ml of 0·025*M* solution of Aliquat 336 in chloroform, stopper the tubes and agitate them for two minutes. Allow the solutions to settle for a further 30 min, then measure the absorbance of the organic phase at 570 mμ, using the aluminium-free solution as reference. The phase should be filtered through glass wool into the spectrophotometer cells to remove traces of water.

The calibration curve prepared under these conditions is linear over this concentration range, *i.e.*, 0·11–0·54 ppm Al. The molar absorptivity at 570 $m\mu$ is 42000 which corresponds to a sensitivity index (Sandell[5]) of 0 00064 $\mu g/cm^2$ for an absorbance of 0 001.

The sensitivity of the reaction may, however, be improved by extracting the complex from a large aqueous volume into a smaller volume of organic solvent. The extent of extraction of Calmagite itself is dependent on the volume ratio, but, if the reagent blank solution is prepared under similar conditions, this problem is eliminated.

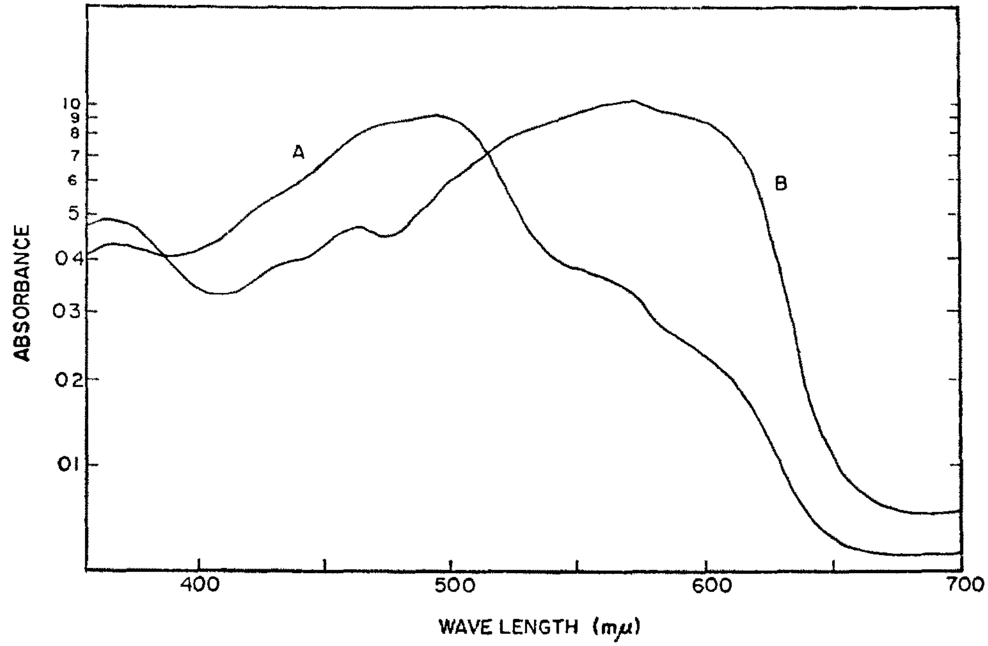

FIG. 1.—Absorbance of Calmagite and its aluminium complex after extraction with 0·05M solution of Aliquot 336 in chloroform, pH 8·7.
Measured in 1-cm cells with 0 05M Aliquot 336 in chloroform as reference.
A—8 × $10^{-5}M$ Calmagite
B—8 × $10^{-5}M$ Calmagite + 16 × $10^{-5}M$ aluminium.

RESULTS AND DISCUSSION

Effect of foreign ions

Several cations, notably transition metal ions, also react with Calmagite under the proposed conditions of the aluminium determination and thus cause interference with the method. It has previously been demonstrated, however,[6] that cyanide and EDTA may be used as general masking agents in the spectrophotometric determination of aluminium by extraction from alkaline medium with 8-hydroxyquinoline. Although no extensive examination of the effects of foreign ions on the present method has been undertaken, some preliminary experiments were carried out to demonstrate that these masking agents were also effective in this system. In the presence of $10^{-2}M$ cyanide and 5 × $10^{-3}M$ EDTA (added as the calcium-EDTA complex with excess of calcium ions present to prevent the possibility of EDTA complexing the aluminium), the effects of 60-fold molar excesses of such ions as Cu, Ni, Zn, Cd and Pb on the determination of 0·22 ppm of Al were $<\pm 10\%$. Undoubtedly, any interference by such ions could be totally eliminated by the addition of appropriate amounts of these masking agents. It may be preferable for the purpose of elimination of interferences to carry out the determination of aluminium at a pH higher than 8·6 even though this will result in some decrease in sensitivity. Taking pK_a for hydrocyanic acid as 9·3,[7] it is obvious that only approximately 17% of the cyanide added will be present as CN^- at pH 8·6, *cf.* 50% at pH 9·3 and 83% at pH 10·0. Thus the effectiveness of a given amount of sodium cyanide as a masking agent will increase considerably with a relatively small increase in pH. Also, at pH 9·3 (8·6) the logarithms of the conditional stability constants[8] of various metal–EDTA complexes are approximately: Al 3·8(5·0), Ca 9·6(9·0), Zn 14·6(14·5), Cd 14·6(14·5), Cu 16·4(16·3), Fe(III) 13·8(13·8), Co(II) 14·8(14·6), so the effectiveness of EDTA as a masking agent would also be increased by an increase in pH.

The effects of a number of common anions on the absorbance due to aluminium were also examined. At the 80-fold molar excess level none of the anions examined, *viz.*, fluoride, chloride, bromide, iodide, perchlorate, borate, nitrate, nitrite, sulphate, sulphite, thiosulphate, bisulphate, carbonate, bicarbonate, cyanide, thiocyanate, phosphate, acetate, formate and citrate, caused a significant change. Fluoride and phosphate were then examined at the 800-fold molar excess level but no interference was found. Probably fluoride complexing of aluminium is prevented by the masking action of the borate buffer used.

For practical purposes, it would be preferable to replace the stoppered vials which were used for this exploratory work by separatory funnels. It may also be convenient and time-saving to prepare a composite solution containing appropriate amounts of buffer, Calmagite and masking agents.

Nature of complex

The composition of the anionic aluminium–Calmagite complex has been investigated by the standard spectrophotometric methods, *viz.*, mole-ratio,[9] slope-ratio[10] and continuous variations procedures.[11,12] As discussed above, it was known that the Calmagite sample used was only 60% pure and solution concentration were, therefore, corrected in a suitable manner. Also, to avoid the further complication that at pH 8·6 significant amounts of both H_2D^- and HD^{2-} are present in solution, these experiments were carried out at pH 9·5, under which conditions virtually all Calmagite is present as HD^{2-}.

The slope-ratio studies indicated a 3:1 Calmagite·Al complex and the mole-ratio studies a complex of greater than 2.1 molar proportions. The maximum of the continuous variations curves appeared in the region of 2:1 molar proportions, but the shape of these curves was such that the position of the maximum was difficult to determine. On the basis of these experiments and by comparison with previous observations with a very similar reagent,[13] it seems reasonable to suggest that the complex formed between aluminium and Calmagite at pH 8·6 is of 1:3 molar proportions.

CONCLUSION

The sensitivity of this reaction, coupled with its simplicity, suggests that it may find application to the determination of aluminium in numerous circumstances. The solvent extraction step permits concentration so that the sensitivity may be increased beyond that of reactions carried out totally in the aqueous phase. Furthermore, the ease of elimination of interferences indicates that it should also have advantages in selectivity over existing methods.

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Zusammenfassung—Calmagit wird als empfindliches spektrophotometrisches Reagens für Aluminium mit $\varepsilon_{520nm} = 42000$ vorgeschlagen. Nach Reaktion in wäßriger Phase bei pH 8,6 wird der Komplex aus Metall und Reagens durch Bildung eines Ionenassoziats mit einem quartären Ammoniumsalz in Chloroform extrahiert. Die Methode wird durch die haufig vorkommenden Anionen nicht gestort; kationische Störungen konnen mit Cyanid und EDTA als Maskierungsmittel beseitigt werden.

Résumé—On propose la calmagite comme réactif spectrophotométrique sensible pour l'aluminium, $\varepsilon_{570m\mu} = 42000$. Après réaction en phase aqueuse à pH 8,6, le complexe métal-réactif est extrait en chloroforme par formation d'un complexe d'association ionique avec un sel d'ammonium quaternaire. La méthode est exempte d'interférence par les anions communs, et l'on peut éliminer les interférences cationiques par l'emploi de cyanure et d'EDTA comme agents de dissimulation.

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DETERMINATION OF NITROGEN IN AN ALUMINIUM-KILLED STEEL BY AN ISOTOPE-DILUTION METHOD USING $Al^{15}N$

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Summary—Nitrogen in an aluminium-killed steel was determined by an isotope-dilution method using synthesized aluminium nitride enriched with ^{15}N. The results were in agreement with those obtained by chemical determination, whereas the vacuum fusion method with iron and platinum baths, and the isotope-dilution method using gaseous ^{15}N-enriched nitrogen, did not give accurate results.

THE determination of nitrogen in steels by the vacuum fusion method is considered less accurate than that by the chemical method except in the case of samples containing stable nitrides such as Si_3N_4. The difference between the results from the two methods decreases if the extraction time is increased, but if the nitrogen content is low (<100 ppm) negative deviations may still arise in the vacuum fusion results, either because of incomplete extraction of nitrogen,[1,2] or because the nitrogen is determined by difference and the error is therefore determined by the error of the least accurate measurement involved. We have reported elsewhere that the methods of vacuum fusion and isotope-dilution with gaseous ^{15}N-enriched nitrogen gave the same results but that these were lower than the certified chemical values.[3] We suggested that an isotope dilution method in which the isotope is added to a molten sample in a crucible would give accurate nitrogen values.

Pearce and Masson[4–6] fused a steel sample in a degassed graphite crucible and allowed it to equilibrate over a period of 30 min with a measured quantity of nitrogen enriched with ^{15}N at a gas-circulation temperature of 1600 or 1650°. Notwithstanding generally accepted evidence to the contrary, they reported that good agreement was observed for several types of steels between the results of the chemical, the isotope-dilution, and the vacuum fusion methods when the vacuum fusion analyses were performed at 2100 or 2240°

Orolova and Vitol' determined the nitrogen in an alloyed steel and other refractory metals, including niobium[7] They prepared a master alloy of niobium powder saturated with ^{15}N at 900° for 4 or 5 hr. The isotopic composition of the nitrogen liberated from the master alloy was calculated on the basis of the amounts of the nitrogen introduced and that initially contained in the powder. They showed a comparison of the data with the chemical method only in the case of the niobium samples, in which the isotope-dilution values were 0·02% lower than the chemical values. Their determination of the nitrogen content and of the isotopic concentration in the master alloy is not described

In the present work, aluminium nitride was used as master alloy for the determination of nitrogen in an aluminium-killed steel. Aluminium nitride is a very common constituent of steels and under the conditions of vacuum fusion analysis for steel samples is found to be decomposed to nitrogen.[2] Aluminium nitride is also easily decomposed by sodium hydroxide solutions and to yield ammonia. Hence the chemical (Kjeldahl) method can be applied to the determination of nitrogen in aluminium nitride. The isotopic composition of the gaseous nitrogen was measured and obtained by oxidation of the ammonia redistilled from the titrated solution.

EXPERIMENTAL

Preparation of ^{15}N-enriched aluminium nitride

Metallic aluminium grains were heated at 1300° in an atmosphere of ammonia obtained from ^{15}N-enriched ammonium sulphate and sodium hydroxide. After 1 hr of heating the aluminium nitride was crushed to powder in an agate mortar. The aluminium grains were covered with the pulverized crude aluminium nitride and heated again. This procedure was repeated several times. Figure 1 shows the apparatus used, of which the ammonia preparation tube is a modification of Clusius and Effenberger's tube.[8] The nitrogen content of the aluminium nitride was determined chemically by potentiometric titration; the coefficient of variation was 1% (4 determinations). The concentration of nitrogen-15 was measured by means of a mass spectrometer after redistilling the ammonia and oxidizing it to nitrogen with hypobromous acid.[9] Results on aluminium nitride containing 3% of ^{15}N showed a coefficient of variation of 1% (4 determinations). No change in isotopic composition was observed during these procedures.

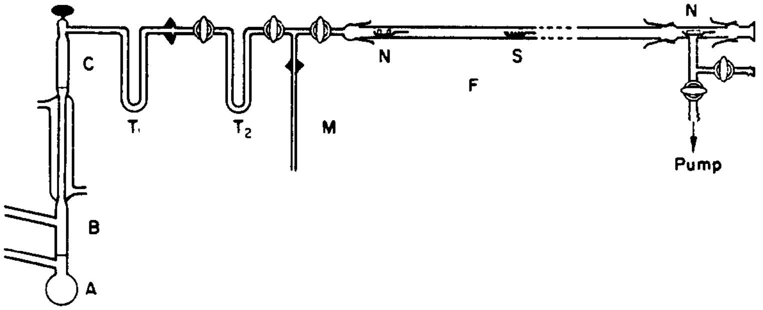


FIG. 1.—Apparatus for preparation of aluminium nitride.
A—^{15}N-enriched $(NH_4)_2SO_4$; *B*—NaOH pellets; *C*—NaOH pellets; T_1—trap for H_2O; T_2—trap for NH_3; *M*—manometer; *F*—furnace; *S*—sample; *N*—metallic sodium boats.

Apparatus

Analyses were made with the aid of a modified isotope-dilution-vacuum fusion apparatus described previously.[10,11] A gas-extraction pump having a rate of 41 l./sec at 10^{-5}–10^{-2} mmHg was used. A by-pass tube was inserted from the collecting-tube to the end of the sample-loading arm on the furnace in order to circulate the gas in the system to equilibrate with isotope-enriched nitrogen. A Toepler pump, a sampling tube for isotope concentration measurement, and an isotope gas inlet were also inserted.

The collecting-tube normally used had a capacity of 83 2 ml, and was connected to an oil manometer for pressure measurement. The oil used was Dow-Corning Silicone No. 703. The volume of the tube was calibrated by means of a gas-burette with a reading error of ±1 %. The manometer sensitivity for nitrogen was 0·00728 mg/mm. Two Pirani gauges were used for continuously monitoring the pressure at the collecting-tube and the intermediate collecting-tube.

Carbon monoxide and hydrogen evolved from the samples were oxidized to carbon dioxide and water respectively, by circulating the gas mixture over heated copper(II) oxide. Water was absorbed with phosphorus pentoxide and carbon dioxide was frozen out in a liquid-nitrogen trap. The residual gas was assumed to be nitrogen, which was collected by means of the Toepler pump for mass spectrometric measurement in the isotope-dilution analyses.

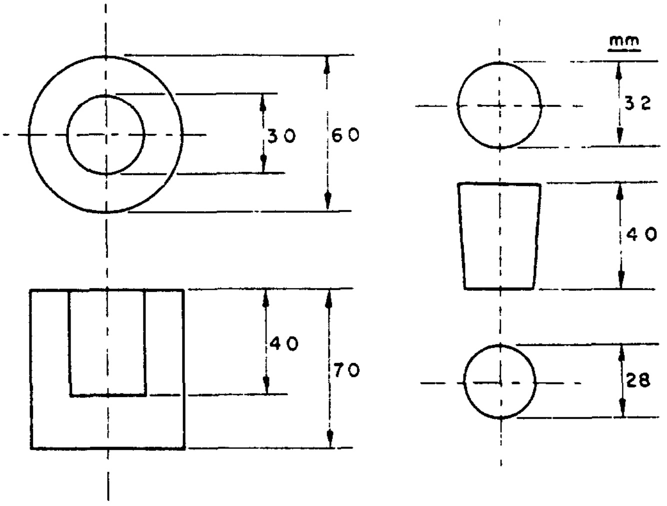
The isotope-dilution method using gaseous nitrogen was employed, and a cock was inserted between the furnace and the extraction pump in order to increase the pressure in the furnace for the purpose of simulating the conditions of analysis used by Pearce, in which there may be considerable flow-resistance between the furnace and the circulation pump.

A modified CEC-103A type mass spectrometer was used to determine the isotopic composition of the extracted nitrogen, the ion currents at *m/e* 28, 29, and 30 all being used. The ^{15}N-enriched ammonium sulphate used was obtained from the Institute of Physical and Chemical Research, Tokyo, Japan, and ^{15}N-enriched nitrogen from the Bio-Rad Laboratories, Richmond, California, U.S.A.

Sample material

The aluminium-killed steel used was that used in the cooperative study of the Japan Society for the Promotion of Sciences, 19th Committee, Gas Analysis Sub-Committee. Its composition was C, 0·09%; Si, 0·01%; Mn, 0·26%; P, 0·006%; S, 0·032%; Cu, 0·14%, Al, 0·010%.

Before analysis, specimens were cut from a sample rod, smoothed with fine files, rinsed in light petroleum and allowed to dry in air. Specimens for the aluminium nitride isotope-dilution analysis were cut as shown in Fig. 2, with the aid of a lathe without using any cutting oil. After rinsing and drying, a measured quantity of ^{15}N-enriched aluminium nitride was placed in the cavity of portion *A*, and portion *B* was then plugged into the cavity to about half its depth and tapped lightly so that it would not become dislodged.



Portion A Portion B

FIG. 2.—Sample for the isotope-dilution method using Al^{15}N.

Procedures

Vacuum fusion analysis. The conventional analysis at 1650° for steel samples was used; 15 g of electrolytic iron were used as bath metal. To investigate the effect of the crucible temperature, analysis was done at 1850° with the same quantity of electrolytic iron. Ogahara[12] and Dallmann[13] have recommended platinum as a good bath for the nitrogen analysis, so analyses were also done with 15 g of platinum at 1750° and 2100°, the highest temperature for the apparatus used. In all of these experiments the blank rate was negligible.

After the crucible assembly had been degassed at 2200° or 2300°, the bath metal was dropped into the crucible at the temperature of analyses. Degassing took 1–2 hr in the case of iron, and 15 min for platinum. A sample was then dropped in and the evolved gas was oxidized, trapped, and measured by means of the oil manometer.

Isotope-dilution analysis. All analyses were done at 1650° with an iron bath. In the method using ^{15}N-enriched nitrogen gas the influence of the pressure in the furnace was investigated by means of a cock inserted between the furnace and the extraction pump. To avoid the effect of glow discharge through the heating elements, the pressure was kept under 10^{-3} mmHg.

After the crucible had been degassed and the bath metal dropped into the crucible, the temperature was set to the gas-extraction temperature for a period of 1 hr and any residual gas in the metal was pumped off until the blank rate was negligible. A measured quantity of ^{15}N-enriched nitrogen was introduced into the system, and the specimen was immediately added to the crucible. After 30 min circulation the gas was collected, oxidized, trapped, and transferred to a sampling tube for mass spectrometric analysis. The residual gas evolved after 30 min was also examined.

In the method employing ^{15}N-enriched aluminium nitride, two varieties of aluminium nitride were used, one containing about 3% ^{15}N and the other about 60% ^{15}N. The nitrogen content of the aluminium nitride and its isotopic composition were determined each time before use. A sample with aluminium nitride was dropped into the degassed bath metal in the graphite crucible. The evolved gas was circulated in the system for 30 min and was then introduced into the analysing system to get rid of carbon monoxide and hydrogen, and transferred to a sampling tube. The residual gas evolved after 30 min was similarly treated. In all these experiments the blank rate was negligible.

Chemical analysis. All analyses were performed according to the conventional method, except that a trapping flask containing 20 ml of 0.01*N* sulphuric acid was attached at the exit of the digestion flask, and this solution and the sample solution were steam-distilled with sodium hydroxide solution.

RESULTS AND DISCUSSION

Table I shows the results of the isotope-dilution analysis. In the analysis of sample 1, the ^{15}N concentration of the gas collected in the first 30 min was the same as that of the gas collected during the next 15 min. This shows that isotopic equilibrium was established in both gas and liquid phases in the furnace in the initial 30 min. In the analysis of sample 4, however, the ^{15}N concentration increased gradually and isotopic equilibrium was not established even after 45 min. This change in composition indicates that there was gradual decomposition of aluminium nitride in the sample and the possibility of incomplete extraction of nitrogen caused by graphite deposited in the bath metal through prolonged heating. The nitrogen value for sample 4 was apparently extraordinarily high.

TABLE I.—COMPARISON OF RESULTS OF NITROGEN DETERMINATION BY ^{15}N ISOTOPE-DILUTION

Sample	Weight, *g*	^{15}N added, *mg*	Nitrogen collected during 0–30 min *mm* oil†	% ^{15}N	30–45 min *mm* oil†	% ^{15}N	45–60 min *mm* oil†	% ^{15}N†	Nitrogen content, *ppm*
1	2.05	0.657*	17.1	2.40	0.6	2.40	0.0	—	70
4	2.11	0.720*	18.3	1.84	1.5	2.77	0.6	2.95	—
5	2.77	0.0735‡	19.3	42.7	0.4	6.0	0.2	—	38
7	1.94	0.0954‡	10.0	59.0	0.3	14.8	0.2	—	33
9	1.88	0.660¶	12.7	35.1	0.8	33.0	—	—	69

* Added as AlN (3.7% ^{15}N).

† 1.0 *mm* oil ≡ 7.28 μg of nitrogen.

‡ Added as $^{15}N_2$ (90.8% ^{15}N)

¶ Added as AlN (58.2% ^{15}N).

In the analysis of sample 5 the extracted gas was progressively diluted with the natural nitrogen from the melted sample. This is evidence that isotopic equilibrium was not attained in the system. The result was 32 ppm lower than that for sample 1.

In the analysis of sample 7, a cock was inserted between the furnace and the extraction pump, and the pressure in the furnace was increased. Progressive dilution with natural nitrogen from the melted sample was again observed. The nitrogen value was similar to that of sample 5.

With sample 9, for which the ^{15}N-rich nitride was used, isotopic equilibrium was established in 30 min.

The results obtained are summarized in Table II. The values obtained by the chemical method and the isotope-dilution method using ^{15}N-enriched aluminium nitride are in good agreement, while the results by the other methods are markedly different.

TABLE II —NITROGEN CONTENT OF ALUMINIUM-KILLED STEEL

Method	^{15}N added as	Extraction temperature, °C	Bath metal	Nitrogen value, *ppm*	Mean *ppm*
Vacuum fusion		1650	Fe	27, 36, 32, 35	33
		1850	Fe	21, 33, 37, 42	33
		1750	Pt	51, 50, 48, 47	49
		2100	Pt	46, 44, 40, 40	43
Isotope-dilution	$^{15}N_2$	1650	Fe	38, 37, 33, 42	38
	$Al^{15}N$	1650	Fe	65, 70, 68, 69	68
Chemical				59, 69, 63, 67, 60	64

In the vacuum fusion analysis using a platinum bath, the nitrogen values obtained at 2100° were lower than those for 1750°, owing to the increased solubility of nitrogen in molten platinum. In the iron-bath method, results obtained at 1850° were scattered and a longer extraction time was needed than at 1650°, for the same reason as for the platinum bath. Although an increase of the extraction temperature promotes the dissociation of nitride, it does not necessarily result in an increase in the quantity of nitrogen extracted.

The isotope-dilution method using gaseous nitrogen did not give any correct nitrogen values. Isotopic equilibrium was not established in 30 min even when a cock was inserted, and during gas circulation in the system the ^{15}N-enriched nitrogen introduced was either absorbed or reacted with graphite to form cyanogen, resulting in positive errors.

The isotope-dilution method using ^{15}N-enriched aluminium nitride is accurate and simple, and eliminates the errors encountered from gas absorption and incomplete gas extraction in the vacuum fusion method. The application of this method to samples containing chemically stable nitrides is now being investigated.

Zusammenfassung—Stickstoff wurde in einem aluminium-beruhigten Stahl durch Isotopenverdunnung bestimmt, unter Verwendung synthetischen, mit ^{15}N angereicherten Aluminiumnitrids. Die Ergebnisse stimmen mit denen chemischer Analysen uberein; dagegen lieferten Vakuumschmelzen mit Eisen- und Platinbädern sowie die Isotopenverdunnungsmethode mit gasförmigem, ^{15}N-angereichertem Stickstoff keine genauen Ergebnisse.

Résumé—On a dosé l'azote dans un acier désoxydé à l'aluminium par une méthode de dilution isotopique utilisant un nitrure d'aluminium synthétisé enrichi en ^{15}N. Les résultats sont en accord avec ceux obtenus par détermination chimique, tandis que la methode de fusion sous vide avec des bains de fer et de platine et la méthode de dilution isotopique utilisant de l'azote gazeux enrichi en ^{15}N ne donnent pas de résultats précis.

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RAPID VISUAL COMPLEXIMETRIC TITRATION OF CALCIUM IN NATURAL WATERS

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Summary—Visual compleximetric methods for the titration of calcium in the presence of magnesium have been based either on masking the magnesium or using an indirect indicator procedure, *e.g.*, the system Zn–EGTA–Zincon. In the proposed method these two approaches are combined. Zn–EGTA complex is added to the mixture and the zinc liberated in the calcium replacement reaction is titrated with EGTA after the magnesium has been masked with fluoride ion.

Despite the widespread acceptance of the compleximetric method for the determination of temporary and permanent hardness in water, there is as yet no truly satisfactory visual procedure for the determination of calcium in the presence of magnesium.

The standard method whereby the sum of calcium and magnesium is titrated by EDTA at pH 10 gives an accurate value for "total" hardness, but determination of calcium in a second sample by titration at pH ≥ 12 leads to erroneous results owing to co-precipitation of some of the calcium on the magnesium hydroxide. This situation has been fully reviewed and several possibilities for improvement have been suggested.[1,2]

More recently ethyleneglycol bis(β-aminoethyl ether)-*N*,*N*,*N'*,*N'*-tetra-acetic acid (EGTA)[3] has been used as a selective chelating agent for the titration of calcium in the presence of magnesium.[4] Although the difference in the stability constants of the calcium and magnesium EGTA complexes ($\log K_{\text{CaY}} = 11{\cdot}0$, $\log K_{\text{MgY}} = 5{\cdot}2$) is sufficient for a selective titration of calcium in the presence of (soluble) magnesium the development of a satisfactory visual method has been handicapped by the lack of a calcium-specific indicator. The main emphasis, therefore, has been on instrumental detection of the end-point.

Schmid and Reilley, in their original method[4] utilized a mercury/mercury(II)–EGTA electrode for the potentiometric detection of the end-point. This type of detection system has also been used to monitor the titration of calcium in the presence of magnesium with coulometrically generated EGTA.[5] Amperometric indication of the end-points has been employed by Monnier and his co-workers[6,7] in the sequential titration of calcium and magnesium. In addition, a fluorimetric procedure has been described.[8] It would also appear that enthalpimetric detection of the end-point[9] is feasible, although little attention has been paid to this method up to the present time.

In spite of the experimental simplicity of most of these techniques, a visual end-point is usually to be preferred and several groups of workers have examined different possibilities.

Two main lines of approach have been made. In the first are found those methods which have concentrated on selective masking of one of the components, usually magnesium. Thus Burg and Conaghan[10] have developed a method for the sequential titration of calcium and magnesium which is basically a modification of the earlier EDTA procedure. Calcium is titrated at pH 13 with EGTA, Calcon being used as indicator and the magnesium masked with tartaric acid. The pH is then lowered to 10 and the magnesium is titrated with EDTA. In Přibil's procedure, magnesium is titrated with *trans*-1,2-diaminocyclohexane-*N*,*N*,*N′*,*N′*-tetra-acetic acid (DCTA) after the calcium has been masked with a measured excess of EGTA.[11]

The other main line of approach has been by an indirect method using the system zinc–EGTA/Zincon to sensitize the end-point.[12,13] The measured stability constant of zinc–EGTA is 12·8.[13] Thus to displace the equilibrium of the replacement reaction

$$Ca^{2+} + ZnEGTA^{2-} \rightleftarrows CaEGTA^{2-} + Zn^{2+}$$

towards the right-hand side so that the end-point reaction

$$\underset{\text{orange–yellow}}{Zn^{2+} + HIn^{3-}} \rightleftarrows \underset{\text{blue}}{ZnIn^{2-}} + H^{+}$$

can occur, it is necessary to add auxiliary complexing agents (*e.g.*, ammonia in the buffer system).

Because calcium and magnesium do not form complexes with Zincon, the end-point is marked by the transition from blue to orange–yellow as zinc–EGTA is formed. Unfortunately this indicator system is very sensitive to changes in buffer composition and concentration. In addition the presence of conventional masking agents cannot readily be tolerated.

In the present study, the calcium/magnesium mixture is treated with an excess of zinc–EGTA complex in an ammonia buffer at pH 10 so that the replacement reaction occurs. After the magnesium has been suitably masked, the liberated zinc ion is titrated with EGTA, Zincon being used as indicator.

The selection of conditions for masking the magnesium is critical. The masking agent must form a stronger complex with magnesium than EGTA, *i.e.*, $\log K_{MgX} > 6$. At the same time the calcium and zinc complexes of the masking agent must be much weaker than the corresponding EGTA complexes and must be soluble.

DEVELOPMENT OF METHOD

The residual solution after the replacement reaction contains calcium–EGTA complex, unreacted zinc–EGTA complex and unchelated magnesium and zinc ions. The selection of a masking agent for the magnesium ions is complicated by the fact that most of the conventional masking agents for magnesium also form insoluble zinc salts. Fluoride ion was chosen ($\log K = 8\ 15$) and masking of the magnesium was found to be complete when the dielectric constant of the solution was lowered by the addition of 25% of ethanol.

Initial results showed considerable inconsistency, owing to the influence of the composition and nature of the buffer, and to reaction between the calcium complex and fluoride ions.

Earlier observations that the end-point for this titration is critically dependent on the nature and concentration of the buffer system were confirmed. When the anion of the ammonia buffer system was changed from chloride to acetate, improved results were obtained, provided all other experimental parameters were fixed. The dependence of the experimental result on time of standing indicated that there was a slow reaction between calcium–EGTA and fluoride ion. The absence of reaction between zinc–EGTA and fluoride ion (unlikely in view of the high stability constant of zinc–EGTA) was confirmed. It was apparent, therefore, that this interference would be influenced by the ratio of magnesium to calcium, *i.e.*, a large excess of fluoride beyond the amount required to mask magnesium would cause a significant error. Thus for a given concentration of magnesium in a calcium/magnesium mixture there exists a range of fluoride concentrations beyond which interference will occur. The limits were found experimentally for calcium:magnesium ratios from 10:1 to 1:50. The results obtained are shown in Fig. 1. For most natural waters the ratio magnesium:calcium lies in the range from 1:5 to 1:2. Thus from the total concentration of magnesium and calcium, determined by separate titration, a rough estimate of the magnesium concentration can be made. By reference to Fig. 1 the required amount of fluoride can be found. Moreover it can be seen from Fig. 1 that the tolerance to fluoride is quite appreciable over the range of concentrations of calcium and magnesium shown by most water samples. Thus 3·5 ml of 1*M* fluoride, as recommended in the general procedure, will effectively mask up to 10 mg of magnesium and should prove to be entirely satisfactory for almost all water analyses. Even if 25 mg of magnesium were present the error would only be approximately +2%. The error only becomes appreciable, *i.e.*, >5%, when the Mg:Ca ratio is >50:1.

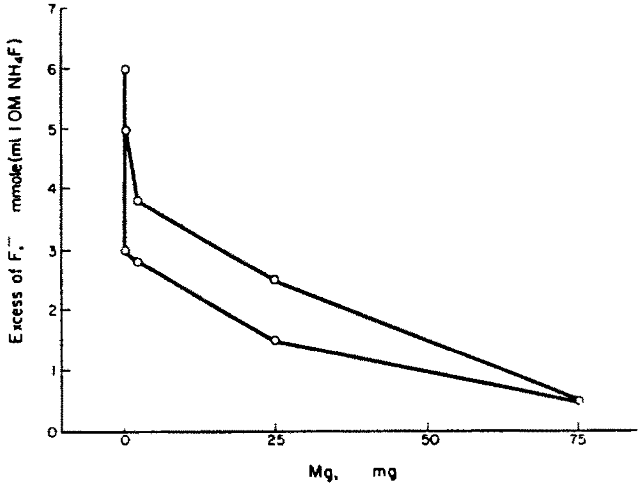

FIG. 1.—Permissible ranges of fluoride for masking magnesium. The two curves give the upper and lower limits of fluoride for a given amount of magnesium.

EXPERIMENTAL

Reagents

Ethyleneglycol bis(β-aminoethyl ether)-N,N,N,′N′-*tetra-acetic acid*, 0·01*M*. Prepare by dissolving 7·6 g of the acid in 10 ml of 4*M* sodium hydroxide and 10 ml of distilled water and diluting to 2 l., Standardize with standard calcium solution (see *Procedure*).

Calcium solutions (0·1*M and* 0·01*M*). Dissolve 5·0045 g of pure calcium carbonate in hydrochloric acid and dilute the solution to 500 ml (0·1*M*). Prepare the 0·01*M* solution by dilution.

Magnesium solutions (0·1*M and* 0·01*M*) Dissolve 12·325 g of analytical reagent grade magnesium sulphate heptahydrate, in distilled water and dilute to 500 ml (0·1*M*). Prepare the 0·01*M* solution by dilution.

Ammonia/ammonium acetate buffer, pH 10·3. Dissolve 50·5 g of ammonium acetate in 300 ml of water and add 100 ml of concentrated ammonia solution. Adjust the pH to the exact value with ammonia and dilute to 500 ml. Use analytical grade reagents.

Buffered zinc–EGTA complex, 0·05*M*. Prepare by mixing equivalent amounts of 0·2*M* zinc sulphate and 0·2*M* EGTA (by titration, with Zincon as indicator) and adding an equal volume of buffer solution.

Ammonium fluoride, 1·0*M*. Dissolve 18·52 g of ammonium fluoride (analytical grade) in distilled water and dilute to 500 ml.

Zincon indicator solution. Dissolve 0·013 g of Zincon (*o*-[2-(2-hydroxy-5-sulphophenylazo)-benzylidene hydrazino] benzoic acid) in 0·5 ml of 4*N* sodium hydroxide, dilute to 10 ml, and store in a refrigerator. The solution is stable for approximately one week.

Procedure

To 25–50 ml of the sample solution, containing 4–12 mg of calcium and 0–15 mg of magnesium add 8 ml of the buffered zinc complex. Shake the solution and add 3·5 ml of 1*M* fluoride solution. (The volume of fluoride solution needed can be found from Fig. 1.) Add enough absolute alcohol to give a 25% v/v solution of it, and then 10 drops of indicator. About 2 min after the addition of the fluoride, titrate the solution with standard EGTA till the colour changes from blue to orange.

Standardization of EGTA solution. To 25·00 ml of 0·01*M* calcium solution, add 30 ml of water and 8 ml of the buffered zinc complex. Shake the solution and add ethanol (to give 25% v/v) followed by 10 drops of Zincon indicator. Titrate with EGTA until the last trace of blue disappears and the solution becomes pale orange-yellow.

RESULTS AND DISCUSSION

A representative selection of results obtained is shown in Table I.

Table I.

Calcium Taken, *mg*	 Found, *mg*	Difference, %	Mg:Ca ratio
2·00	2·01	+0·5	1:1
4·01	4·10	+2·3	1:2
8·02	8·18	+2·0	1:4
12·02	12·17	+1·3	1:6
4·01	4·00	−0·2	1:10
4·01	4·10	+2·3	1:2
4·01	4·03	+0·5	1:1
4·01	3·98	−0·8	2·1
4·01	3·94	−1·8	5:1
4·01	3·93	−2·0	10·1

Examination of interferences

Some possibly interfering ions were examined. No interference was found from Fe^{3+}, Pb^{2+}, PO_4^{3-} and SO_4^{2-} whereas Cu^{2+} (>0·5 ppm), Co^{2+} (>1 ppm), and Ni^{2+} (>2 ppm) influenced the end-point. Mn^{2+} (>5 ppm) and Al^{3+} (>3 ppm) also interfered. Although common masking agents, *e.g.*, CN^-, cannot be used in this procedure, this is no disadvantage as the interfering elements are generally not present to this extent in natural waters.

It is clear that the use of a masking agent for the magnesium improves the sharpness of the end-point and that the slow reaction of fluoride with calcium–EGTA does not cause any appreciable error provided the titration is carried out as recommended. The recoveries obtained (Table I) show that only at Mg:Ca ratios $\geq$ 5:1 does the fluoride ion cause any noticeable error.

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Zusammenfassung—Visuelle komplexometrische Vorschriften zur Titration von Calcium neben Magnesium beruhten entweder auf Maskierung des Magnesiums oder Benutzung einer indirekten Indikation, z B mit dem System Zn–EGTA–Zincon In der vorgeschlagenen Vorschrift werden diese beiden Verfahren kombiniert Zu dem Gemisch wird der Zn–EGTA-Komplex gegeben und das durch Calcium verdrangte Zink nach Maskierung des Magnesiums mit Fluorid mittels EGTA titriert.

Résumé—On a basé des méthodes complexométriques visuelles pour le titrage du calcium en présence de magnesium, soit sur la dissimulation du magnésium, soit sur l'emploi d'une technique indirecte avec indicateur, par exemple le système Zn–EGTA–Zincon Dans la méthode proposée, ces deux voies sont combinées. On ajoute le complexe Zn–EGTA au mélange et le zinc libéré dans la réaction de remplacement par le calcium est titré à l'EGTA après que le magnésium ait été dissimule par l'ion fluorure.

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ANION-EXCHANGE BEHAVIOUR OF THE PLATINUM METALS AND GOLD IN HYDROCHLORIC ACID–ORGANIC SOLVENT MEDIA

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Summary—The anion-exchange characteristics of the platinum metals and gold in hydrochloric acid media are described. The distribution coefficients of these elements were measured on the strongly basic anion-exchange resin Dowex 1 × 8 in mixtures of hydrochloric acid with water and several organic solvents, *i.e.*, dimethylformamide, acetone, tetrahydrofuran, dioxan, methanol, acetic acid and pyridine. Based on these data the conditions most suitable for quantitative separation are indicated and discussed.

DUE to the fact that the platinum metals and gold readily form stable anionic chloride complexes most of these elements are strongly retained by strongly basic anion-exchange resins from pure aqueous hydrochloric acid media. The least strongly adsorbed platinum metals are the tervalent ions of iridium and rhodium. Consequently most methods so far reported for the anion-exchange separation of the platinum metals from one another are concerned with separations of iridium and/or rhodium from the rest of the platinum metals.[1–9]

The strong adsorption of the anionic chloride complex of gold has also been employed for the anion-exchange separation of this element from a number of metal ions.[10–24] For the elution of the adsorbed gold, mixed aqueous–organic solvent solutions containing hydrochloric acid have been used.[13] Except for this latter application no attempt has so far been made to investigate systematically the anion-exchange behaviour of gold and the platinum metals in hydrochloric acid–organic solvent media. In order to obtain a much more complete picture of the adsorption characteristics and separation possibilities of these elements in organic solvent media, the work presented in this paper was performed, using the most frequently employed anion-exchange resin Dowex 1 in mixtures of 7 organic solvents with hydrochloric acid. For this purpose the effect of increasing concentration of organic solvent and the effect of acidity on the adsorption of the platinum metals and gold were investigated by measuring the distribution coefficients in numerous mixtures of varying composition. From the distribution data thus obtained, the possibilities of separating the elements from one another are indicated and discussed.

EXPERIMENTAL

Reagents

Ion-exchange resin. The air-dried strongly basic anion-exchanger Dowex 1 × 8 (100–200 mesh, chloride form) was used for the column and batch experiments.

Standard solutions. Weighed amounts of the chlorides of ammonium tetrachloroplatinate(II), hexachloroplatinic acid, palladium(II) chloride, ammonium hexachloropalladate(IV), ammonium hexachloro-osmate(IV), potassium hexachloroiridate(III), ammonium hexachloroiridate(IV)

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Table I.—Distribution coefficients of platinum metals and gold on Dowex 1 in pure aqueous hydrochloric acid solutions

	Final HCl concn, *M*				
Metal ion	12	9	6	3	1·2
Pt(II)	480	710	2800	5000	10^4
Pt(IV)	430	870	1900	3600	10^4
Pd(II)	32	50	120	500	1300
Pd(IV)	33	55	80	350	1600
Os(IV)	1100	3700	4800	10^4	10^4
Ir(III)	1·9	1·5	2·3	7·7	16
Ir(IV)	700	1500	2600	7000	10^4
Ru(III)	11	25	90	300	650
Ru(IV)	15	25	70	420	820
Rh(III)	1·6	1·6	2·7	7	20
Au(III)	470	10^3	3500	10^4	10^4

Table II.—Distribution coefficients of platinum metals and gold on Dowex 1 in dimethylformamide–hydrochloric acid mixtures

	Final HCl concn., *M*, in the presence of dimethylformamide (% *v/v*)			
Metal ion	9 (25)	6 (50)	3 (75)	0·0 (100)
Pt(II)	115	60	30	0·7
Pt(IV)	100	40	17	0·7
Pd(II)	11	15	18	>1500
Pd(IV)	11	15	23	<1
Os(IV)	230	120	26	1·0
Ir(III)	1·2	1·4	2·0	1
Ir(IV)	160	50	23	0·5
Ru(III)	1·7	1·1	1·1	0·3
Ru(IV)	1·3	0·9	<2	1·3
Rh(III)	2·2	1·8	1·8	0·7
Au(III)	420	90	7	0·7

Table III.—Distribution coefficients of platinum metals and gold on Dowex 1 in acetone–hydrochloric acid mixtures

	Final HCl concn, *M*, in the presence of acetone (% *v/v*)			
Metal ion	9 (25)	6 (50)	3 (75)	1·2 (90)
Pt(II)	250	>800	>700	>1000
Pt(IV)	200	>1000	>250	>1500
Pd(II)	27	44	150	400
Pd(IV)	26	44	150	600
Os(IV)	>500	>750	>600	>1000
Ir(III)	3*	30	>800	>1000
Ir(IV)	>500†	>800†	>700†	>1000†
Ru(III)	90	>700	>700	>1300
Ru(IV)	60	>800	>1800	>3000
Rh(III)	3	30	900	>1000
Au(III)	380	130	7	2

* Partial oxidation of iridium to its higher oxidation state occurs in this medium.

† Partial reduction of iridium to its lower oxidation state occurs in these media.

TABLE IV.—DISTRIBUTION COEFFICIENTS OF PLATINUM METALS AND GOLD ON DOWEX 1 IN TETRAHYDROFURAN–HYDROCHLORIC ACID MIXTURES

Metal ion	Final HCl concn., *M*, in the presence of tetrahydrofuran (% v/v) 9 (25)	6 (50)	3 (75)	1.2 (90)
Pt(II)	900	>500	400	10^3
Pt(IV)	700	500	600	$>10^3$
Pd(II)	30	60	120	250
Pd(IV)	27	75	120	>400
Os(IV)	1200	750	>900	>800
Ir(III)	3*	30*	400	$>10^3$
Ir(IV)	500	400	>400	>600
Ru(III)	1300†	>500	>500	6000
Ru(IV)	1300†	>700	>1100	>8000
Rh(III)	4	22	260	>600
Au(III)	380	35	2	2

* Partial oxidation of iridium to its higher oxidation state occurs in these media
† In these media distribution coefficients of 60–70 were also measured.

TABLE V.—DISTRIBUTION COEFFICIENTS OF PLATINUM METALS AND GOLD ON DOWEX 1 IN DIOXAN–HYDROCHLORIC ACID MIXTURES

Metal ion	Final HCl concn., *M*, in the presence of dioxan (% v/v) 9 (25)	6 (50)
Pt(II)	390	250
Pt(IV)	285	270
Pd(II)	25	40
Pd(IV)	20	30
Os(IV)	610	600
Ir(III)	2*	10*
Ir(IV)	200†	80†
Ru(III)	20	3
Ru(IV)	19	3
Rh(III)	3	9
Au(III)	310	240

* Partial oxidation of iridium to its higher oxidation state occurs in these media

† Partial reduction of iridium to its lower oxidation state occurs in these media.

TABLE VI.—DISTRIBUTION COEFFICIENTS OF PLATINUM METALS AND GOLD ON DOWEX 1 IN METHANOL–HYDROCHLORIC ACID MIXTURES

Metal ion	Final HCl concn., *M*, in the presence of methanol (% v/v) 9 (25)	6 (50)	3 (75)
Pt(II)	330	>1200	>1500
Pt(IV)	>300	>1100	$>10^3$
Pd(II)	37	130	500
Pd(IV)	40	110	600
Os(IV)	900	>2000	>6000
Ir(III)	3	15	430
Ir(IV)	>640*	1600*	>7000*
Ru(III)	39	>900	>4000
Ru(IV)	45	>1100	>5000
Rh(III)	2.5	28	300
Au(III)	>1200	850	500

* Partial reduction of iridium to its lower oxidation state occurs in these media

TABLE VII.—DISTRIBUTION COEFFICIENTS OF PLATINUM METALS AND GOLD ON DOWEX 1 IN ACETIC ACID–HYDROCHLORIC ACID MIXTURES

Metal ion	Final HCl concn., M, in the presence of acetic acid (% v/v) 9 (25)	6 (50)	3 (75)
Pt(II)	>2500	10^3	>8000
Pt(IV)	>3000	10^3	>6000
Pd(II)	36	75	400
Pd(IV)	34	75	500
Os(IV)	>2000	>2000	>8000
Ir(III)	2	14	200
Ir(IV)	>1200*	1500*	>7000*
Ru(III)	32	>600	>3000
Ru(IV)	43	>550	>6000
Rh(III)	3	17	210
Au(III)	>10^3	750	400

* Partial reduction of iridium to its lower oxidation state occurs in these media.

TABLE VIII.—DISTRIBUTION COEFFICIENTS OF PLATINUM METALS AND GOLD ON DOWEX 1 IN PYRIDINE–HYDROCHLORIC ACID MIXTURES

Metal ion	Final HCl concn., M, in the presence of pyridine (% v/v) 9 (25)	6 (50)	3 (75)
Pt(II)	35	2	1
Pt(IV)	32	1	1
Pd(II)	11	1	1
Pd(IV)	9	<1.5	<2
Os(IV)	50	40	5
Ir(III)	1	1	<1
Ir(IV)	1	1	<1*
Ru(III)	4	2.5	2
Ru(IV)	2	1	1
Rh(III)	1	1	1
Au(III)	>100†	>50†	<1

* Partial reduction of iridium to its lower oxidation state occurs in this medium

† Gold is virtually insoluble in these media.

ruthenium(III) chloride hydrate, ammonium hexachlororuthenate(IV), ammonium hexachlororhodate(III) and tetrachloroauric acid were dissolved in 12M hydrochloric acid to give solutions containing not less than 0.5 mg of element/ml

Solvents. The reagent-grade pure organic solvents used were dimethylformamide, acetone, tetrahydrofuran, dioxan, methanol, acetic acid and pyridine.

Determination of distribution coefficients

Most of the distribution coefficients of the platinum metals and gold were determined by the column method[25], 1 g of air-dried resin being used in each case. Other distribution data were obtained by the batch method.[26]

For the detection and determination of the platinum metals and gold, suitable colour-forming reagents have been used.[27]

RESULTS AND DISCUSSION

In Tables I–VIII are shown the distribution coefficients of the platinum metals and gold in the various media that have been investigated. Although the adsorption

TABLE IX—SEPARATION FACTORS OF PLATINUM METALS AND GOLD ON DOWEX 1 IN HYDROCHLORIC ACID SOLUTIONS

Metal ion pairs	Separation factors
Pt(II)–Pd(II)	14(W), 15(W), 12(DMF), >1000(DMF), 9(A), >19(A), >30(THF), 7(D), 16(D), 9(M), >70(AA)
Pt(IV)–Pd(II)	13(W), 17(W), 10(DMF), >1000(DMF), 7(A), >23(A), >23(THF), 7(D), 12(D), ~8(M), >85(AA)
Pt(II)–Pd(IV)	13(W), 15(W), 12(DMF), 10(A), >19(A), 36(THF), 20(D), 8(D), 8(M), 73(AA).
Pt(IV)–Pd(IV)	13(W), 16(W), 10(DMF), 8(A), >23(A), >28(THF), 9(D), 15(D), 8(M), 88(A)
Pt(II)–Os(IV)	20(P)
Pt(IV)–Os(IV)	20(P)
Pt(II)–Ir(III)	250(W), 470(W), 1200(W), 1200(W), 1000(W), 95(DMF), 41(DMF), 14(DMF), 83(A), >28(A), >30(THF), 15(THF), 180(D), 23(D), 110(M), ~80(M), >1250(AA), 75(AA), 35(P).
Pt(IV)–Ir(III)	220(W), 580(W), 1300(W), 900(W), 1000(W), 83(DMF), 30(DMF), 8(DMF), 67(A), >33(A), >23(THF), 170(THF), 130(D), 25(D), >100(M), >74(M), >1500(AA), 76(AA), 30(P)
Pt(II)–Ru(III)	44(W), 28(W), 68(DMF), 55(DMF), 27(DMF), 19(D), 83(D), 8.5(M), 80(AA)
Pt(IV)–Ru(III)	39(W), 35(W), 59(DMF), 36(DMF), 15(DMF), 15(D), 90(D), 8(M), 90(AA)
Pt(II)–Ru(IV)	32(W), 28(W), 77(DMF), 67(DMF), 20(D), 83(D), 7(M), >60(AA)
Pt(IV)–Ru(IV)	29(W), 35(W), 88(DMF), 44(DMF), 15(D), 90(D), >7(M), >70(AA)
Pt(II)–Rh(III)	300(W), 440(W), 1000(W), 730(W), 1000(W), 52(DMF), 32(DMF), 16(DMF), 83(A), >33(A), >222(THF), 20(THF), 130(D), 28(D), 130(M), 43(M), 830(AA), 60(AA), 35(P)
Pt(IV)–Rh(III)	270(W), 540(W), 700(W), 530(W), 1000(W), 45(DMF), 23(DMF), 67(A), >39(A), >175(THF), 23(THF), 100(D), 30(D), >120(M), 40(M), >1000(AA), 63(AA), 32(P)
Pt(II)–Au(III)	>100(A), >500(A), 13(THF), >200(THF), >500(THF), >25(P).
Pt(IV)–Au(III)	36(A), >700(A), 14(THF), ~300(THF), >500(THF), >25(P)
Pd(II)–Os(IV)	37(W), 60(W), 21(DMF), 8(DMF), >1500(DMF), >18(A), >17(A), 40(THF), 24(D), 15(D), >24(M), >55(AA), 5(P), 40(P)
Pd(IV)–Os(IV)	33(W), 55(W), 21(DMF), 7(DMF), >18(A), >17(A), 44(THF), 32(D), 20(D), >22(M), >59(AA), 5(P), >26(P).
Pd(II)-Ir(III)	16(W), 33(W), 52(W), 66(W), 84(W), 9(DMF), 11(DMF), >1500(DMF), 9(A), 10(THF), 4(D), 12(M), 9(M), 18(AA), 5(AA)
Pd(IV)–Ir(III)	17(W), 37(W), 35(W), 45(W), 105(W), 9(DMF), 10(DMF), 11(DMF), 9(A), 9(THF), 7(M), 13(M), 5(AA), 17(AA)
Pd(II)–Ir(IV)	24(W), 30(W), 15(DMF), >3000(DMF), >18(A), 17(THF), 8(D), >17(M), >33(AA), 5(P)
Pd(IV)–Ir(IV)	21(W), 27(W), 15(DMF), >19(A), >18(A), 19(THF), 10(D), >16(M), ~35(AA), 6(P).
Pd(II)–Ru(III)	6(DMF), 14(DMF), 16(DMF), >5000(DMF), >16(A)
Pd(IV)–Ru(III)	6(DMF), 13(DMF), 21(DMF), >16(A).
Pd(II)–Ru(IV)	>9(DMF), >1200(DMF), 18(A)
Pd(IV)–Ru(IV)	>11(DMF), 18(A)
Pd(II)–Rh(III)	19(W), 31(W), 44(W), 75(W), 65(W), 5(DMF), 8(DMF), 10(DMF), >2100(DMF), 9(A), 7(THF), 8(D), 15(M), 7(M), 12(AA), 4(AA), 10(P)
Pd(IV)–Rh(III)	21(W), 34(W), 30(W), 51(W), 80(W), 5(DMF), 8(DMF), 13(DMF), 9(A), 7(THF), 6(D), 16(M), 4(M), 11(AA), 4(AA), 9(P)
Pd(II)–Au(III)	14(W), 20(W), 38(DMF), 6(DMF), >2100(DMF), 25(A), 200(A), 60(THF), 125(THF), 12(D), 6(D), >31(M), >28(A), 10(P), >50(P)
Pd(IV)–Au(III)	14(W), 18(W), 38(DMF), 6(DMF), 25(A), 300(A), 60(THF), >200(THF), 16(D), 8(D), >29(M), >31(AA), 11(P), >33(P)
Os(IV)–Ir(III)	580(W), 2500(W), 2100(W), >1000(W), 1000(W), 190(DMF), 90(DMF), 13(DMF), >17(A), >25(A), 400(THF), 25(THF), 280(D), 54(D), >300(M), >130(M), >1000(AA), >160(AA), 48(P), 40(P)
Os(IV)–Ir(IV)	39(P)

Table IX. (*cont.*)

Metal ion pairs	Separation factors
Os(IV)–Ru(III)	100(W), 150(W), 140(DMF), 110(DMF), 24(DMF), 30(D), 200(D), >23(M), >62(AA)
Os(IV)–Ru(IV)	73(W), 150(W), 170(DMF), 140(DMF), >13(DMF), 32(D), 200(D), >20(M), >46(AA), 24(P), 40(P)
Os(IV)–Rh(III)	690(W), 2300(W), 1800(W), 1000(W), >1000(W), 100(DMF), 70(DMF), 14(DMF), >170(A), >29(A), 300(THF), 34(THF), 200(D), 70(D), 36(M), 71(M), 670(AA), 130(AA), 48(P), 40(P)
Os(IV)–Au(III)	87(A), >500(A), 21(THF), >450(THF), >400(THF)
Ir(III)–Ru(III)	6(W), 17(W), 39(W), 42(W), 23(A), 17(THF), 13(M), 60(M), 16(AA), 43(AA)
Ir(III)–Ru(IV)	8(W), 17(W), 30(W), 51(W), 37(W), >27(A), >23(THF), 15(M), >77(M), 21(AA), >43(AA)
Ir(III)–Au(III)	250(W), 670(W), 1500(W), 1000(W), >1000(W), 350(DMF), 64(DMF), 130(A), 4 3(A), 110(A), >500(A), 130(THF), >200(THF), >500(THF), 130(D), 22(D), 380(M), 57(M), > 500(AA), 54(AA), > 100(P), >50(P)
Ir(IV)–Ru(III)	65(W), 60(W), 94(DMF), 45(DMF), 21(DMF), 10(D), 27(D), >16(M), 37(AA), 14(P)
Ir(IV)–Ru(IV)	47(W), 60(W), 120(DMF), >11(DMF), 10(D), 27(D), 14(M), >28(AA), 28(P)
Ir(IV)–Rh(III)	430(W), 940(W), 960(W), 1000(W), 1000(W), 73(DMF), 28(DMF), 13(DMF), >170(A), >27(A), 125(THF), >18(THF), 67(D), 9(D), >26(M), 57(M), >400(AA), 90(AA), 57(P).
Ir(IV)–Au(III)	>100(A), > 500(A), >11(THF), >200(THF), > 300(THF), > 50(P)
Ru(III)–Rh(III)	7(W), 16(W), 33(W), 46(W), 32(W), >23(A), > 20(THF), >23(THF), 7(D), 16(M), >[illegible]2(M), 43(AA), >35(AA)
Ru(IV)–Rh(III)	9(W), 16(W), 26(W), 60(W), 41(W), 20(A), 27(A), 20(THF), >32(THF), 6(D), 18(M), > 41(M), 53(AA), > 32(AA)
Ru(III)–Au(III)	43(W), 40(W), 250(DMF), 82(DMF), >100(A), >650(A), > 14(THF), >250(THF), 3000(THF), 15(D), 80(D), 31(M), >31(AA), > 25(P)
Ru(IV)–Au(III)	31(W), 40(W), 320(DMF), 100(DMF), > 260(A), > 1500(A), >20(THF), >700(THF), >4000(THF), 16(D), 80(D), 37(M), > 23(AA), >50(P).
Rh(III)–Au(III)	290(W), 625(W), 1300(W), >1000(W), 1000(W), 190(DMF), 50(DMF), 130(A), 4 3(A), >500(A), 95(THF), 130(THF), > 300(THF), 100(D), 27(D), >150(M), 17(M), > 125(AA), 21(AA), 21(AA), >100(P), >50(P).

W = water, DMF = dimethylformamide, A = acetone, THF = tetrahydrofuran, D = dioxan, M = methanol, AA = acetic acid, P = pyridine

of these elements on strongly basic anion-exchange resins from pure aqueous hydrochloric acid solutions has previously been described by several investigators,[3,4,28–31] the adsorption values are recorded in Table I so that these data can readily be compared with those in Tables II–VIII The distribution coefficients of the platinum metals recorded in Table I are in good agreement with those that have been measured earlier. In the case of the adsorption of gold, however, all values are lower by about one order of magnitude at high hydrochloric acid concentrations

In order to avoid a rather lengthy discussion of the separation possibilities of the platinum metals and gold in the various media listed in Tables I–VIII, numerous experimentally determined separation factors of many pairs of metal ions in these mixtures are recorded in Table IX From these results it is seen that in the mixed aqueous–organic solvent systems higher separation factors are found and hence better separation possibilities exist than in pure aqueous hydrochloric acid systems The separation factor of any given pair of ions is the ratio of the distribution coefficients of the two elements as measured under identical experimental conditions.

Difficulties in determining the separation factors have been encountered in all those systems containing iridium, which when present in the tervalent state is partly oxidized to the quadrivalent form which shows different adsorption characteristics. The same is true when iridium(IV) is present; this is partly reduced to the tervalent state. Therefore separations involving this element cannot readily be carried out.

Separations that cannot be performed by the application of pure aqueous hydrochloric acid systems include those of Pt(II)-Os(IV), Pt(IV)-Os(IV), Pt(II)-Au(III), Pt(IV)-Au(III), Pd(II)-Ru(III), Pd(II)-Ru(IV), Pd(IV)-Ru(IV), Os(IV)-Ir(IV), Os(IV)-Au(III) and Ir(IV)-Au(III). These separations can, however, effectively be carried out in the presence of organic solvents (see Table IX). This once more illustrates the usefulness of organic solvents for ion-exchange separations of metal ions. In the case of separations involving the elution of gold with acetone or tetrahydrofuran each containing hydrochloric acid, the combined ion-exchange-solvent extraction (CIESE) principle described earlier[32] makes these separations possible.

Zusammenfassung—Das Anionenaustauschverhalten der Platinmetalle und Gold in salzsauren Medien wird beschrieben. Die Verteilungskoeffizienten dieser Elemente wurden an dem stark basischen Anionenaustauschharz Dowex 1 × 8 in Gemischen von Salzsaure mit Wasser und mehreren organischen Losungsmitteln wie Dimethylformamid, Aceton, Tetrahydrofuran, Dioxan, Methanol, Essigsaure und Pyridin gemessen. Auf Grund dieser Daten werden die zur quantitativen Trennung am besten geeigneten Bedingungen angegeben und diskutiert.

Résumé—On décrit, du point de vue échange anionique, les caractéristiques des métaux du groupe du platine et de l'or, en milieu acide chlorhydrique. Les coefficients de partage de ces élements ont été mesurés sur la résine échangeuse d'anions fortement basique Dowex 1 × 8 dans des mélanges d'acide chlorhydrique avec l'eau et plusieurs solvants organiques, c'est-à-dire diméthylformamide, acetone, tétrahydrofuran, dioxane, methanol, acide acétique et pyridine. En se basant sur ces données, on indique les conditions convenant le mieux à la séparation quantitative et en discute.

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SHORT COMMUNICATIONS

Argentometric coulometric titration of thioacetamide

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RECENTLY amperometric titrations of silver[1] and of copper(I)[2] with thioacetamide (TAA) have been investigated as methods for the determination of TAA. Other methods for determining TAA include its potentiometric titration of silver,[3] its titration with chloramine-T,[4] and its titration with iodate[5] The purpose of our investigation was to examine the coulometric titration of TAA with electrogenerated silver. The method was tested in a solution containing both ammonia and sodium hydroxide because the reaction of silver with TAA is reported to be rapid and quantitative in this medium [1,3] A potentiometric end-point was used since it had been successfully used in the volumetric titration.[3]

EXPERIMENTAL

Apparatus

The coulometric cell contained a silver foil generating electrode (6 cm^2 area), a platinum wire auxiliary electrode separated from the titration solution by a tube with a sintered glass disc, a silver-silver sulphide indicator electrode, a saturated calomel reference electrode (SCE) and tubing for purging the titration solution with nitrogen The indicator electrode was prepared by soaking a commercial-type silver electrode in 20% sodium sulphide solution It was further preconditioned by several "dummy" titrations of TAA aliquots. The current was supplied by a Model IV Sargent Coulometric Current Source and potential measurements were made with a Corning Model 7 pH Meter.

Reagents

All solutions were prepared from reagent grade chemicals. The TAA solutions were standardized by the method of Bush, Zuehlke, and Ballard[3]

Procedure

Fifty ml of solution, 0·1M in both sodium hydroxide and ammonia, were purged with nitrogen for 15 min in the coulometric cell. The silver generating electrode was pretreated by dipping it in concentrated nitric acid and then rinsing it well in distilled water. An aliquot of TAA solution containing between 0·2 and 3 mg of TAA was added to the cell and the titration was performed with a current of either 9·05 or 19·3 mA. Nitrogen purging was continued during the titration The potential of the indicator electrode was recorded as a function of microequivalents added and a potential of approx −0·3 V *vs*. SCE was taken as the end-point.

RESULTS AND DISCUSSION

Six determinations were made on identical aliquots containing 1·878 mg of TAA, with an average result of 1·870 mg and a standard deviation of 0·0051 mg. Results of analyses of a number of samples,

TABLE I.—RESULTS OF COULOMETRIC TITRATION

TAA, *mg*		Difference, *mg*
Taken	Found	
0·188	0·186	−0·002
0·435	0·431	−0·004
0·869	0·864	−0·005
1·391	1·380	−0·011
1·756	1·751	−0·005
2·174	2·164	−0·010
2·608	2·606	−0·002

given in Table I, indicate an accuracy comparable to that reported for the amperometric methods [1,8] A consistent negative error which appears independent of sample size was noted

A typical titration curve is shown in Fig 1. The potential readings before the equivalence point varied somewhat with the pretreatment given the indicator electrode. The curve shown was obtained after several titrations with the same indicator electrode.

A number of factors which affect the titration were investigated It was found that the cleaning of the silver generating electrode was quite important Although at the end of one titration the electrode surface appears metallic and free from silver sulphide, if used again without cleaning it rapidly blackens and high results are obtained This indicated that traces of silver sulphide on the electrode cause further surface precipitation, and when the surface is completely coated, oxidation of silver sulphide possibly occurs Prior cleaning with nitric acid was found effective in preventing this blackening during the titration

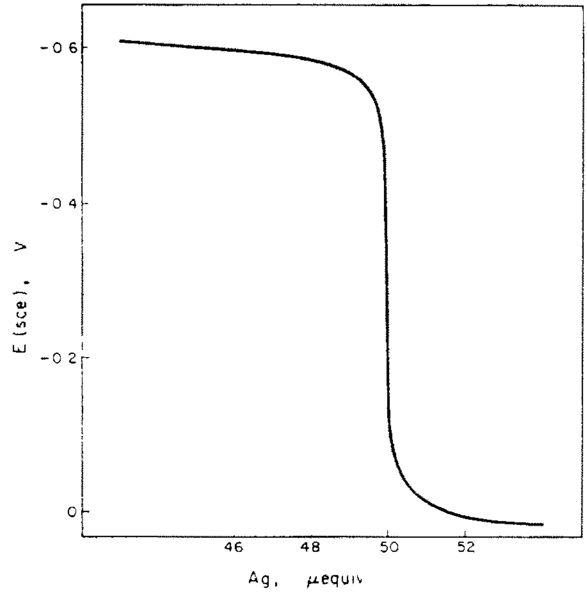

FIG. 1.—Coulometric titration curve for 0 0250 mmole of TAA in 50 ml of 0·1M NH_3/0 1M NaOH

The potential of the indicator electrode was found to drift slowly near the equivalence point and several minutes were required to obtain steady readings A similar effect was reported[6] in the titration of sulphide under the same conditions More rapid stirring and shaking of the electrode had no apparent effect on the time required to obtain steady readings.

The presence of traces of oxygen was found to produce low results In one experiment the TAA was allowed to stand for 30 min in the alkaline solution with no nitrogen purge prior to titration. The titration result was low by 14% On repeating the experiment with a nitrogen purge during the 30 min, the titration result was within the accuracy indicated in Table I. This indicates that the air oxidation of TAA occurs rapidly in alkaline solution

On varying the sample size above a few mg it was found that the silver generating electrode darkened during the titration and high results were obtained It appeared that the electrode was becoming coated with silver sulphide and that a possible side-reaction was the oxidation of silver sulphide. This problem was not encountered with samples of less than 3 mg.

The effect of increasing the ammonia concentration was tested. Accurate results were obtained although the size of the potential break decreased Increasing the sodium hydroxide concentration had the effect of accelerating the air oxidation of TAA

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Summary—The coulometric determination of thioacetamide (TAA) with electrogenerated silver is described. The titration is done in a solution 0·1*M* in both ammonia and sodium hydroxide, and the end-point is detected potentiometrically with a silver–silver sulphide electrode. On repeat analyses of approx. 2-mg samples of TAA an average error of −0·4% (relative standard deviation 0·25%) was obtained. Important steps in the procedure include cleaning the silver generating electrode in nitric acid before each titration, purging well with nitrogen to remove oxygen, and not using too large a sample.

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Résumé—On décrit le dosage coulométrique du thioacétamide (TAA) par l'argent produit électriquement. Le titrage est effectué dans une solution 0,1*N* en ammoniaque et en soude, et le point de fin de dosage est décelé potentiométriquement par une électrode argent-sulfure d'argent. Par des analyses répétées d'échantillons d'environ 2 mg de TAA, on a obtenu une erreur moyenne de −0,4% (écart type relatif 0,25%). Les points importants de la technique comprennent le nettoyage de l'électrode productrice d'argent dans l'acide nitrique avant chaque titrage, la bonne purge à l'azote pour éliminer l'oxygène et l'emploi d'échantillons pas trop importants.

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COPPER(III) was first reported in 1844 and its history up to 1925 has been reviewed by Votis.[1] Votis,[1] Malaprade[2] and Malatesta[3] have established beyond doubt that copper(II) may be oxidized by potassium persulphate to copper(III) which is stabilized by co-ordination with a suitable anion such as periodate or tellurate.

The first use of copper(III) as an oxidant in titrimetry appears to be due to Beck, who used it for the titrimetric determination of some reducing sugars,[4,5] glycerol,[6] amino-acids[7] and proteins.[8] He also deduced the constitution of proteins from characteristic curves obtained by differential titration of proteins with copper(III) solution.[9]

The direct titrimetric method at room temperature as recommended by Beck suffers from serious limitations. The end-point was indicated by the appearance of a transient green colour stable for 30 sec. He used glucose as a primary standard During the present work it was observed that the appearance of the transient green colour is not a true indication of the end-point. Keyworth and Stone[10] also found Beck's method for detection of the end-point to be unsuitable and hence adopted

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In the present work the oxidation of some sugars has been undertaken and the use of copper(III) as an oxidant studied in detail

EXPERIMENTAL

Reagents

All reagents used were of analytical grade.

Preparation of copper(III) solution Jenšovsky[11] and Beck[3] used potassium persulphate to oxidize copper(II) in the presence of stabilizing ions, and removed the excess of persulphate by boiling the solution for about ½ hr As we have used the iodometric method for the analysis, the complete removal of unused persulphate is very important To this end we have adopted the following procedure for the preparation of potassium ditelluratocuprate(III) ($K_5H_4[Cu(TeO_6)_2]$) solution Copper sulphate (1 561 g), potassium tellurite (3 173 g), potassium persulphate (4 220 g) and potassium hydroxide (8 0 g) are treated with *ca* 80 ml of water The order of addition is not important The mixture is shaken thoroughly and then heated on a hot-plate In about 20 min the boiling mixture becomes intensely red and the boiling is continued for 15 min more for completion of the reaction The mixture is then cooled and filtered (porosity 4 sintered-glass crucible) and the solution is diluted to 100 ml.

The persulphate used is just sufficient to oxidize the copper(II) and tellurite to copper(III) and tellurate and is therefore completely removed during boiling If an excess of persulphate is used boiling for a longer time is necessary for its complete decomposition The absence of persulphate in the prepared solution can be ascertained by acidifying about 1 ml of the solution with dilute sulphuric acid till the red colour is completely discharged and copper(III) converted into copper(II), adding 5 ml of 0 5*M* sodium bicarbonate and 2 ml of 5% potassium iodide solution, letting stand for 2 min and then adding a little starch solution A blue colour indicates the presence of persulphate

It was found that the final concentration of copper(III), 0 03*M*, is more or less the same provided the potassium persulphate is added in theoretical amount or only in slight excess With the amount of copper(II) taken the copper(III) solution should have been 0 0625*M* The divergence appears to be due to the precipitation of a copper compound during boiling The final concentration of potassium hydroxide in the prepared solution is *ca* 0 7*M*, this is essential because copper(III) is stable only in highly alkaline medium The solution thus obtained is fairly stable and the concentration remains practically unaltered for several months

The use of potassium diperiodatocuprate(III) was precluded by the use of an iodometric method for back-titrating the unconsumed sodium arsenite solution Moreover, the periodate might compete with the copper(III) as oxidant

Procedure

To standardize the copper(III) solution, treat 5 ml of it with 5 ml of 0 02*M* arsenite solution (standardized against iodine solution) Let the mixture stand for 3–4 min and then acidify it with [illegible] 0 5*M* sulphuric acid till the green suspension disappears, resulting in a clear solution which is acidic Add 5 ml of 0 5*M* sodium bicarbonate, and back-titrate the unused arsenite with standard iodine solution (0 01*N*), using starch as indicator Run a blank The acidification with sulphuric acid is necessary because if potassium hydroxide in the mixture is not completely neutralized some of the iodine added during the titration will be consumed by it Addition of excess of bicarbonate is important inasmuch as it helps instantaneous oxidation of the arsenite with iodine and its presence also prohibits the liberation of iodine by copper(II) from the iodide in the iodine solution

For estimation of sugars, add an aliquot (see Table I) to an excess of copper(III) solution, heat the mixture on a hot-plate where necessary for complete oxidation, and determine the unconsumed copper(III) by the method above

The excess of Cu(III) was determined after the copper(III)–sugar mixture had (*a*) stood for 5 min, (*b*) stood for 15 min, (*c*) been boiled and cooled

DISCUSSION

From Table I it is clear that the sugars are oxidized to carbon dioxide and water by heating with an excess of copper(III) solution Arabinose and xylose, which are pentoses, require 20 equivalents per mole; the hexoses glucose, fructose, mannose and galactose consume 24 equivalents sucrose requires 48. They have been estimated on this basis The consumption of less copper(III) at room temperature by these sugars indicates that their oxidation at ordinary temperature is incomplete Beck[4] standardized copper(III) against glucose at room temperature, assuming the consumption of 8

TABLE I.—STOICHIOMETRY OF OXIDATION OF SOME SUGARS BY POTASSIUM DITELLURATOCUPRATE(III)

Sugar taken, *ml*		0·035*M* Cu(III) taken, *ml*	Equivalents of Cu(III) consumed per mole of sugar		
			a	*b*	*c*
0·001*M* Glucose	2 0	4·0	8 0	15 9	24·1; 24·0
					24·0; 24·0
0·001*M* Fructose	2 5	3 0	10·1	18·2	24·1
					24·1
					24·1
0 001*M* Mannose	2 5	3·0	8·5	11·8	24·0
	3·0				24·0
	1·0				24·1
0·0048*M* Galactose	1·0	8 0	11·8	12·9	24·1
	1 5				24·1
	0 5				24·0
0 00099*M* Arabinose	3 0	3·0	8·0		20·1
	4 0				20·0
	2·0				20·0
	1·0				20·0
0·0011*M* Xylose	2·0	2 0	10·1	14·1	20·1
	2·5				20·1
	1·0				20·0
0 0005*M* Sucrose	1·0	3·0	18·0	24·8	48·1
	3·0				48·0
	4·0				48·2

equivalents of Cu(III) per mole of glucose. Our results in Table I indicate that the consumption of copper(III) at room temperature increases with standing time and hence the standardization against glucose cannot be recommended. Beck[6] found that mannose stabilized copper(III) but our observations indicate that this sugar is also oxidizable and can be estimated like the others.

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Summary—The titrimetric determination of glucose, fructose, mannose, galactose, arabinose, xylose and sucrose with potassium ditelluratocuprate(III) is described. On heating, pentoses and hexoses consume 20 and 24 equivalents of copper(III) per mole respectively, and sucrose consumes 48 equivalents.

Résumé—On décrit le dosage titrimétrique des glucose, fructose mannose, galactose, arabinose, xylose et sucrose par le ditelluratocuprate(III) de potassium. Par chauffage, les pentoses et hexoses consomment 20 et 24 équivalents de cuivre(III) par mole respectivement, et le sucrose consomme 48 équivalents.

Zusammenfassung—Die titrimetrische Bestimmung von Glucose, Fructose, Mannose, Galactose, Arabinose, Xylose und Sucrose mit Kaliumditelluratocuprat(III) wird beschrieben. In der Hitze verbrauchen Pentosen und Hexosen 20 bzw. 24 Äquivalente Kupfer(III) pro Mol, Sucrose 48.

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Spectrophotometric titration of bismuth with EDTA

(*Received* 12 *April* 1967. *Accepted* 5 *May* 1967)

THE development of a simple and efficient method for the estimation of phosphate in technical sugar solutions[1,2] made it necessary to determine bismuth. The method was based on the procedure due to Vancea[3] for estimation of phosphate in pure solution; phosphate was precipitated quantitatively by adding a known amount of bismuth at pH ~0·5 and then the excess of bismuth was determined. In the past bismuth has been determined gravimetrically,[4-7] titrimetrically,[8-10] and colorimetrically.[11-13] We have developed a new spectrophotometric titration of bismuth with EDTA, using the iron(III)-salicylate complex as indicator.

EXPERIMENTAL

Reagents

Stock solutions of 0·02*M* bismuth nitrate, iron(III) nitrate and EDTA were made in doubly distilled water. Salicylic acid solution, 0·05*M*, was prepared in 50% ethanol. The bismuth and iron solutions were standardized against the EDTA, thiourea and salicylic acid respectively being used as indicators.

The buffer used was prepared by mixing 100·0 ml of 1·0*M* sodium acetate and 240·0 ml of 1·0*M* nitric acid and diluting to 500 ml with water.

Procedure

Known quantities of the standard solutions of iron and bismuth were transferred by pipette to 25-ml standard flasks, followed by addition of 5 ml of 0·05*M* salicylic acid. The pH was adjusted to 0·5 by addition of 10 ml of sodium acetate-nitric acid buffer. Increasing quantities of 0·02*M* EDTA were then added to the flasks, and enough ethanol to give a final concentration of 20% v/v. The solutions were diluted to the mark with water and mixed. The absorbances were then measured at

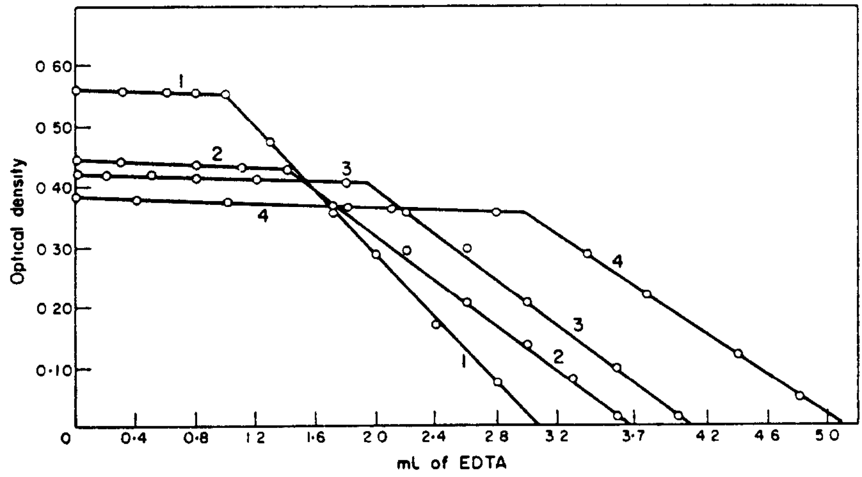

FIG. 1.—Titration curves for bismuth with EDTA in presence of 0·01*M* salicylic acid. Bismuth, μmole: *1*—10; *2*—20; *3*—30; *4*—40.

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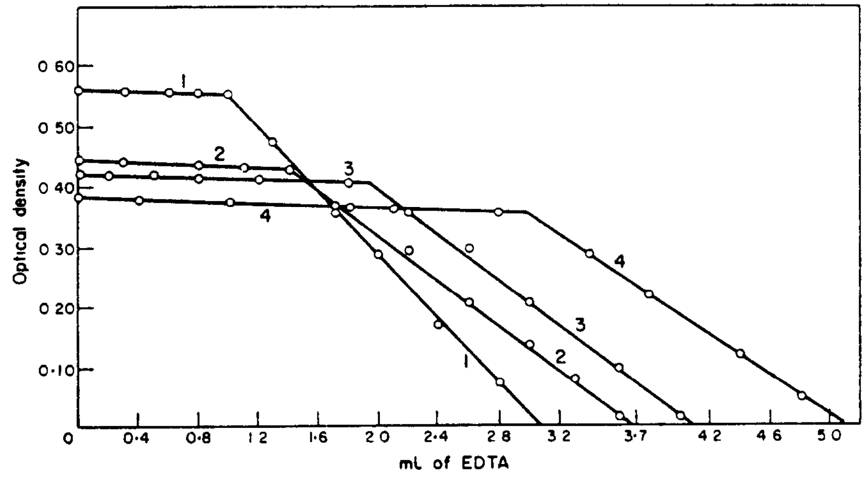

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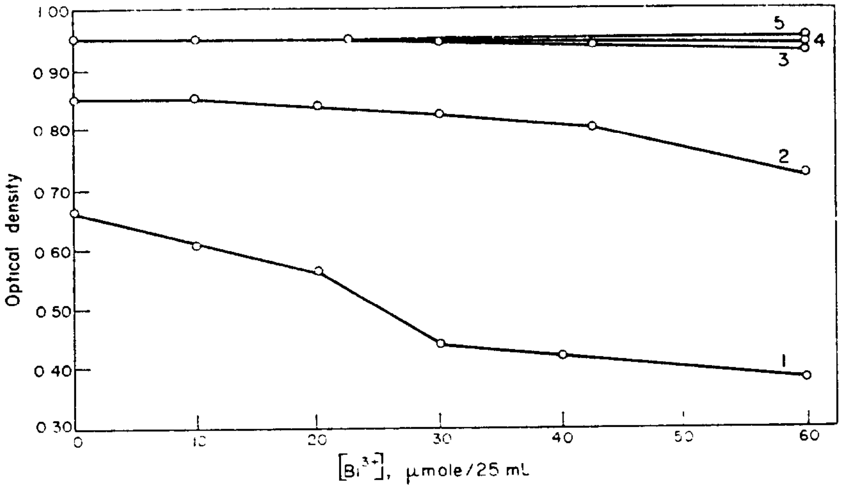

FIG. 2.—Effect of bismuth concentration on absorbance of the iron(III)-salicylate complex, for varying salicylic acid concentrations.
Salicylic acid, *M*: *1*—0·008; *2*—0·016; *3*—0·04, *4*—0·08; *5*—0·10.

520 mμ in 1-cm cells. This stepwise titration had its end-point at the break-point located by extrapolation on a plot of absorbance *vs.* volume of EDTA added. The solution could also be titrated continuously.

Results

Iron(III) forms an intensely violet chelate with salicylic acid. The complex has an absorption maximum at 520 mμ and obeys Beer's law.[19]

A typical set of curves for the titration of bismuth with EDTA is given in Fig. 1. It is of interest to note that the absorbance of the solution decreases with increasing concentration of bismuth, possibly by competition between the iron and bismuth for the salicylate, as indicated by Fig. 2. This decrease in the intensity of the colour does not interfere with the determination, but it can be completely suppressed by increasing the concentration of salicylic acid to 0·1*M*, giving the type of curve shown in Fig. 3.

The range of applicability of the method was examined and the results reported in Table I show that bismuth concentrations ranging from 8 to 500 mg/l can be determined with an error of not more than 1%.

Discussion

It has been reported by Strode *et al.*[20] that the iron(III) salicylate colour in aqueous medium is sensitive to pH, ionic strength and organic solvents. Therefore the pH and the amount of ethanol (20%) were kept constant throughout.

EDTA is known to form soluble complexes with a number of cations[21] at specific pH values. Those cations which are not complexed by EDTA at the low pH used in the present method will therefore not interfere.

During the titration the iron(III)-salicylate and bismuth-EDTA complexes are present before the end-point, and the iron(III)-EDTA complex is also present after it. It is essential in such titrations that the metal to be titrated should not displace metal ions from the indicator complex, and that it should be preferentially titrated, *i.e.*, the metal ion of the indicator complex is not displaced by the titrant until after the equivalence point has been reached. These features depend on the stability constants of the complexes.[22-25] In the present case the equilibria and dissociation constants of the complexes are

$$(\text{Bi-EDTA})^- \rightleftharpoons \text{Bi}^{3+} + (\text{EDTA})^{4-};\ k_1 = 1{\cdot}15 \times 10^{-28}$$
$$(\text{Fe-EDTA})^- \rightleftharpoons \text{Fe}^{3+} + (\text{EDTA})^{4-};\ k_2 = 7{\cdot}93 \times 10^{-26}$$
$$(\text{Fe-Sal})^+ \rightleftharpoons \text{Fe}^{3+} + (\text{Sal})^{2-};\ k_3 = 3{\cdot}98 \times 10^{-16}$$

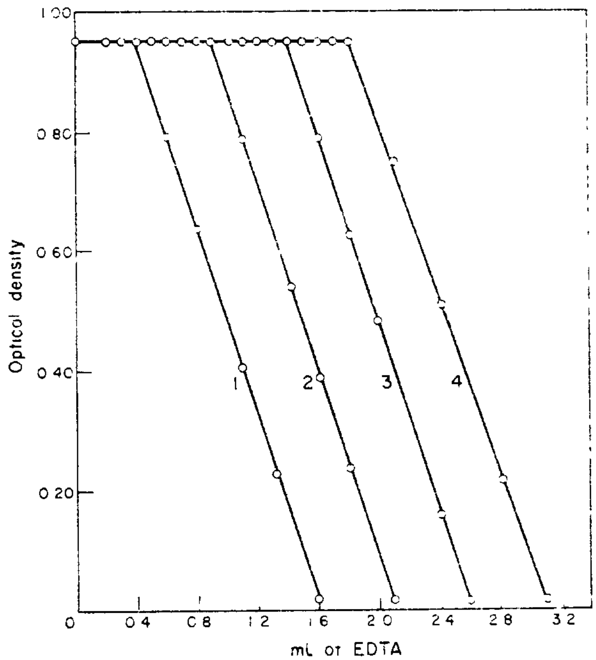

FIG 3.—Titration of bismuth with EDTA in presence of 0.1*M* salicylic acid. Bismuth, μmole *1*—8, *2*—16, *3*—24, *4*—32.

TABLE I.—DETERMINATION OF BISMUTH WITH EDTA

Indicator [Fe(III)], *mg/l*	Bismuth, *mg/l*	
	Taken	Found
90	167.2	168
90	250.8	252
90	334.4	336
90	501.6	499
45	41.8	42
45	83.6	84
45	167.2	167
45	250.8	251
45	334.4	332
45	8.35	8.6

Before the end-point the equilibrium is

$$(\text{Fe–Sal})^{+} + (\text{Bi–EDTA})^{-} \rightleftharpoons (\text{Fe–EDTA})^{-} + \text{Bi}^{3+} + (\text{Sal})^{2-}.$$

The equilibrium constant K_e is given by

$$K_e = \frac{[(\text{Fe–EDTA})^{-}][\text{Bi}^{3+}][\text{Sal}^{2-}]}{[(\text{Fe–Sal})^{-}][(\text{Bi–EDTA})^{-}]} = \frac{k_1 k_3}{k_2}.$$

From the values of the dissociation constants, the value of K_e comes out to be 5.8×10^{-21}, which is extremely small, indicating that the iron(III) salicylate will therefore not react appreciably with the bismuth–EDTA complex. This is confirmed experimentally, since there is no decrease in absorbance before the equivalence point during the titration.

After the equivalence point the operative equilibrium is

$$(\text{Fe–Sal})^{+} + (\text{EDTA})^{4-} \rightleftharpoons (\text{Fe–EDTA})^{-} + (\text{Sal})^{2-}$$

with equilibrium constant

$$K_e' = \frac{[(\text{Fe–EDTA})^{-}][(\text{Sal})^{2-}]}{[(\text{Fe–Sal})^{+}][(\text{EDTA})^{4-}]} = \frac{k_3}{k_2}.$$

The value of K_e' is 5·0 × 10^7, which is very large, and the reaction proceeds quantitatively.

In most of the methods available for bismuth determination the presence of iron(III) interferes, but in the present method this interference is eliminated, as iron(III) in the complexed form acts as the indicator.

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Summary—A new spectrophotometric method for the estimation of bismuth with EDTA, using iron–salicylate complex as the indicator, has been developed. The determinations were carried out by measuring the absorbance at 520 mμ of solutions containing bismuth, iron(III), salicylic acid and various quantities of EDTA, at pH 0·5. It has been shown from the stability constants of the complexes present that before the end-point iron(III) will not react appreciably with the Bi–EDTA complex. The interference from iron(III) in the estimation of bismuth, which is a serious drawback in many other methods, is eliminated in the present method, as iron(III) acts as the indicator.

Zusammenfassung—Es wurde eine neue spektrophotometrische Vorschrift zur Bestimmung von Wismut mit EDTA mit dem Eisen-Salicylatkomplex als Indikator entwickelt. Die Bestimmungen wurden ausgeführt durch Messung der Extinktion bei 520 nm an Lösungen, die Wismut, Eisen(III), Salicylsaure und wechselnde Mengen EDTA bei pH 0,5 enthielten. An Hand der Stabilitatskonstanten der anwesenden Komplexe wurde gezeigt, daß vor dem Endpunkt Eisen(III) nicht merklich mit dem Wismut-EDTA-Komplex reagiert. Die Storung von Eisen bei der Wismutbestimmung, ein wesentlicher Nachteil vieler anderer Methoden, ist bei dieser Vorschrift gegenstandslos, da Eisen(III) als Indikator wirkt.

Résumé—On a élaboré une nouvelle méthode spectrophotométrique pour le dosage du bismuth à l'EDTA, utilisant le complexe fer-salicylate comme indicateur. Les déterminations ont été menées en mesurant l'absorption à 520 mμ de solutions contenant le bismuth, le fer (III), l'acide salicylique et diverses quantités d'EDTA, à pH 0,5. On a montré, à partir des constantes de stabilité des complexes présents, qu'avant le point de virage le fer (III) ne réagit pas de façon appréciable avec le complexe Bi-EDTA. L'interférence du fer (III) dans le dosage du bismuth, qui est un inconvénient sérieux dans de nombreuses autres méthodes, est éliminée dans la présente technique, le fer (III) agissant comme indicateur.

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TALANTA REVIEW*

AMPLIFICATION REACTIONS

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Summary—Amplification methods were first used over 100 years ago but the term only came into general usage during the development of microanalytical techniques. There has been a revived interest in amplification methods during the last few years, for it has been realized that by their application to trace analysis, it is often possible to obtain unusally precise results. The amplification methods available for various cations and anions are reviewed.

AMPLIFICATION (or multiplication) reactions can be defined as reactions in which the normal equivalence is altered in some way so that a more favourable measurement can be made. Probably the first reaction to be given this name was the so-called Leipert reaction[1] for determining iodide. When elemental iodine is released from a solution of iodide by treatment with a suitable oxidizing agent, the reaction proceeds as follows.

$$2I^- + 2Ce^{4+} \rightarrow I_2 + 2Ce^{3+}$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

One equivalent of iodine requires one equivalent of thiosulphate. Similarly, when the iodide ion is titrated with silver nitrate, the same equivalence is obtained. In the Leipert reaction the iodide ion is oxidized quantitatively to iodate by means of bromine water; after the excess of bromine has been destroyed, iodide is added in excess and the following reaction occurs

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

and it is seen that the original equivalence has been amplified six-fold.

It is not correct to call this the Leipert reaction. When Leipert's method was published it had a far-reaching influence on organic microanalysis because hitherto only the gravimetric method could be used for the determination of iodine in organic compounds. Titration with silver was unsuitable because of the very unfavourable equivalence. Leipert first described this method in 1929; further papers appeared in 1933 and 1938. For some inexplicable reason, modern text-books of organic microanalysis quote only the 1938 reference, and it has been remarked that the idea originated

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from Vieböck, who published his method for determining alkoxyl in 1930, based similarly on bromine oxidation of iodide ion.[2] There is no doubt that Leipert preceded Vieböck, but the reaction is much older than the work of either investigator. Winkler,[3] in 1900, appears to have been the first to oxidize iodide to iodate with another halogen; he used chlorine water. Long before Winkler's time permanganate had been used. Hypochlorite was used by Hunter[4] (1909) and bromine by Bugarszky and Horvath[5] (1909). There are many other references in the early literature of this century.

The method of Vieböck and his co-workers, mentioned above for the determination of alkoxyl groups, is based on the reaction given above. In the original method of Zeisel, the alkyl iodide produced was finally converted into silver iodide, which was weighed. In Vieböck's method the methyl iodide is decomposed and the iodide is oxidized as above. This again gives an amplification factor of 6 for the alkoxyl group

$$CH_3O \rightarrow CH_3I \rightarrow IO_3^- \rightarrow 3I_2 \equiv 6CH_3O.$$

Amplification reactions were widely used before this period, but they were not given this special name; examples will be given later. Some attempt should be made to differentiate the two types of reaction that are used and Leipert's and Vieböck's methods provide an example of each. In the Leipert method the constituent required is amplified directly and it is the same constituent which is finally measured. In the Vieböck method it is not the constituent required which is amplified, but the iodide associated with it; it is the latter which is finally measured. The one is a *direct* amplification and the other an *indirect* amplification.

Direct amplification methods are rare and the majority of the amplification methods that are known are based on indirect processes.

It is possible to amplify bromide similarly by oxidizing it to bromate with hypochlorite. This method only received widespread attention after 1937 when it was studied by Kolthoff and Yutzy.[6] The reaction was later applied to the determination of bromine in organic microanalysis and is generally ascribed to Kolthoff and Yutzy, but as with the iodide method the reaction is much older. The first description seems to be due to Weszelszky[7] (1900) and the reaction was later studied by van der Meulen[8] (1931) and by D'Ans and Höfer[9] (1934).

In general, the determination of iodate or bromate is completed simply by adding iodide and titrating the liberated iodine with thiosulphate, but recently a method has been described in which the iodate or bromate is determined polarographically.[10]

OTHER AMPLIFICATION METHODS FOR THE DETERMINATION OF HALIDES

Some other amplification methods for iodide are known, but they are less convenient than the bromine oxidation method. For example, iodide can be converted into iodine cyanide which reacts with thiosulphate.[11]

$$ICN + 2S_2O_3^{2-} + H^+ \rightarrow I^- + HCN + S_4O_6^{2-}$$

It can be seen that in this reaction the normal equivalence is increased two-fold.

Iodide can also be oxidized with periodate[12]

$$I^- + 3IO_4^- \rightarrow 4IO_3^-$$

and the amplification is far better than that of the bromine oxidation reaction.

However, the only convenient way of determining the iodate formed is by back-titration of the unconsumed periodate, which detracts considerably from the value of the method. Quite recently, this reaction has been restudied;[13] by masking of the excess of periodate with molybdate a direct determination seems possible. This particular reaction provides a 24-fold amplification of the original iodide.

Willard and Merritt[14] oxidized iodide to periodate with ozone, which provides an 8-fold amplification, but the procedure is troublesome and does not appear to have been examined further.

It was mentioned earlier that permanganate had been used to oxidize iodide to iodate. The reaction was studied more than a century ago[15] and has continued to be used till fairly recent times.[16] Under appropriate conditions permanganate oxidizes iodide to periodate (in an alkaline medium in the presence of barium ions).[17] Unfortunately the determination has to be completed by back-titration of the unconsumed permanganate.

A useful method for the determination of iodide, in that the amplification proceeds during titration, is based on the reaction[18]

$$I^- + 3ClO^- \rightarrow IO_3^- + 3Cl^-.$$

Standard hypochlorite is used as titrant. At one time it was only possible to determine the end-point potentiometrically, but during the last few years some excellent visual indicators have been discovered.[19]

It is possible to amplify bromide by using conditions under which hypochlorite oxidizes it to hypobromite. Farkas and Lewin[20] studied this reaction. As the extent of amplification is less than in the previous reaction, it is obviously not so advantageous. The most interesting feature of this determination is that the oxidation is done with an excess of standard hypochlorite, which is then destroyed by an excess of standard arsenite, the remaining arsenite being finally titrated with iodine. Presumably standard hypochlorite could be used for this back-titration, and as there is already the excellent method mentioned earlier for determining iodide by direct titration with hypochlorite, it might be of advantage to use hypochlorite as the general titrant in laboratories where these two ions are regularly determined.

It is also possible to determine bromide by formation of BrCN[21] as described previously for iodide, but this reaction again only gives a two-fold amplification.

It is not possible to oxidize chloride to chlorate quantitatively. There are two stages in the reaction, chloride being first oxidized to chlorine which is then converted into hypochlorite and chloride, and this is followed by hypochlorite disproportionating to give chlorate and chloride. It is only possible to amplify chloride by an exchange reaction which will be discussed later.

Hypochlorite also oxidizes iodide to iodate (see p. 358); hence if bromide and iodide are in admixture it is possible to determine both constituents by amplification. One aliquot of the solution is oxidized with hypochlorite to iodide and bromate, and another portion is oxidized with bromine to iodate.[22]

Methods have been described in the literature for the titration of iodate and bromate in admixture.[23] The pH is adjusted to about 4–5, at which only iodate reacts with iodide. The liberated iodine is titrated and the pH is then lowered to about 1. Bromate then reacts with iodide and the titration can be continued. Theoretically, it should be possible to apply these reactions to the determination of iodide and bromide, for it has been seen that both are readily oxidized to the corresponding halates by hypochlorite. Attempts have been made to exploit the reactions, but the results have been unsatisfactory.[24] It would seem that at some stage after oxidation, products are present which may affect the limits of the graded pH ranges. These reactions require a very careful step-wise examination so that the sources of error can be eliminated. It would be of great practical importance if such a method could be developed.

An amplification method for chloride ion, based on an exchange reaction, was first described by Hazlewood and King[25] in 1936. A year later Sendroy[26] published a similar method, apparently independently, for he does not mention the earlier work. It is based on the reaction of silver iodate with chloride ion; the mixed precipitates are filtered off and iodate is determined in the filtrate.

$$AgIO_3 + Cl^- \rightarrow AgCl + IO_3^-$$

Later workers have applied this reaction to the determination of chlorine in organic compounds.[27]

Avaliani recommended mercury(I) iodate[28] for the same purpose and Belcher and Goulden examined mercury(II) iodate.[29]

$$Hg_2(IO_3)_2 + 2Cl^- \rightarrow Hg_2Cl_2 + 2IO_3^-$$

$$Hg(IO_3)_2 + 2Cl^- \rightarrow HgCl_2 + 2IO_3^-$$

The last reaction depends on the formation of the very feebly dissociated mercury(II) chloride and so a second precipitate is not formed as in the other two reactions.

With the silver iodate method, various corrections are applied to allow for solubility and slow reactivity, but Belcher and Goulden showed that the solubility effect can virtually be ignored, for the amount of iodate ion released depresses the solubility of the particular reagent used. They examined all three methods and found that although mercury(II) iodate gave the best results, it could only be used in neutral solution; in acid solution the solubility of the reagent was increased. For general purposes they considered that mercury(I) iodate might be the best for the range of chlorine found in organic compounds in microanalysis.

Lambert and Yasuda[30] recommended silver iodate in a column for the determination of traces of chloride but the lowest concentration of chloride they determined was 30 ppm. High blanks would be expected at lower concentrations. More recently Roberts[31] has tried exchange columns of mercury(I) and mercury(II) iodates and periodates and certain other compounds. He found that with the more soluble compounds blanks were too high, and with the less soluble, the exchange reaction was not quantitative when practicable contact times were used.

APPLICATIONS OF THE IODIDE AND BROMIDE AMPLIFICATION METHODS

Obviously these amplification reactions can be applied outside titrimetric analysis; or they can be applied indirectly to the determination of other substances. The determination of alkoxyl has already been mentioned. In the Unterzaucher method[32] for direct determination of oxygen, the carbon monoxide formed reacts with iodine pentoxide.

$$5CO + I_2O_5 \rightarrow 5CO_2 + I_2$$

As it stands, this reaction is unfavourable for iodimetry and it would be better to measure carbon dioxide, but in Unterzaucher's method the iodine is captured and oxidized to iodate, and the reaction above is amplified 6-fold.

For the determination of iodine in traces, Geilmann and Bartlingck[33] oxidized it to iodate, released the iodine, extracted it into carbon tetrachloride, back-extracted it into sodium hydrogen sulphite solution and then oxidized it to iodate again. This gives a 36-fold amplification and if necessary the process can be continued.

Shah and Qadri[34] applied iodide amplification to the determination of small amounts of nitrogen in organic compounds. After Kjeldahl digestion the solution was passed through two columns of ion-exchange resin, one above the other. The first column contained the resin in the hydroxide form; this removed sulphuric acid and converted the ammonium ions into ammonia solution. The second column contained the resin in the iodide form and converted the ammonia into ammonium iodide which was then amplified. The same principle has been extended to the determination of amides after hydrolysis to ammonium salts.[35]

Traces of boron can be determined by forming the mannitol complex and using the liberated protons to release iodine from a solution of iodide–iodate. The iodine is extracted into carbon tetrachloride. For moderate trace amounts the absorbance of the extracted iodine can be measured directly, but for extremely small amounts the iodine is back-extracted and oxidized to iodate, which is then treated with iodide, the liberated 6-fold amount of iodine being re-extracted into carbon tetrachloride for final measurement.[36]

Applications of the bromide amplification are hard to find, probably because the iodide amplification is simpler. Obviously, the method can be applied for trace determination of bromine, and in one such method the bromate formed, instead of being treated with iodide, is treated with bromide so that six equivalents of bromine are obtained[37]; the bromine is then treated with rosaniline hydrochloride and measured spectrophotometrically.

Methyl bromide in air and in products in which it is used as a fumigant, has been determined by conversion to bromate.[38] A modification of van der Meulen's method[8] is used.

Many years ago in this Department, during the study of methods for the determination of fluoride, the latter was precipitated as lead bromofluoride[39] instead of lead chlorofluoride in order to give an amplification reaction, but the method offered no advantages. Others have since examined this possibility,[40] but presumably have come to the same conclusions, for the method has never come into use.

INDIRECT AMPLIFICATION OF METALS

It was stated earlier that amplification methods had been used for many years without the term being applied. When 8-hydroxyquinoline is used to precipitate metals and the precipitate is determined by titration with bromide–bromate, an *indirect* amplification is obtained.[41]

$$Mg^{2+} + 2C_9H_7NO \rightarrow (C_9H_6NO)_2Mg + 2H^+$$

$$C_9H_7NO + 2Br_2 \rightarrow C_9H_5NOBr_2 + 2HBr$$

One mole of 8-hydroxyquinoline requires 4 equivalents of bromine; 1 mole of complex of bivalent metal requires 8 equivalents of bromine.

Other organic reagents give a similar indirect amplification for various metals when the precipitate is titrated with bromide–bromate. For example, Furman and Flagg[42] applied the reaction of bromine with hydroxylamine to the indirect determination of metals precipitated by reagents containing the oxime group. Copper after precipitation with salicylaldoxime or α-benzoinoxime, and nickel after precipitation with dimethylglyoxime, were determined in this way. Very favourable equivalences were obtained.

As it is possible to determine 8-hydroxyquinoline by oxidation with cerium(IV) perchlorate,[43] it follows that any metal which can be isolated as the 8-hydroxyquinoline complex and which can readily be dissolved, may be determined cerimetrically. The advantage of this procedure is that an abnormally favourable equivalence is obtained, for 1 mole of 8-hydroxyquinoline consumes 29·8 equivalents of cerium(IV) perchlorate. Magnesium[44] and aluminium[45] have been determined by this procedure; it is said that 5 μg of magnesium can be determined satisfactorily.

The reaction is not completely understood and so the procedure is quite empirical. Despite the very favourable amplification of the cerium method, the bromate procedure is to be preferred.

Calcium in organic matter has been determined by precipitating it as the picrolonate, isolating the precipitate, and subjecting it to rapid wet combustion. The carbon dioxide is measured manometrically. The amplification is 20-fold and as little as 0·2 mg of calcium can be determined satisfactorily.[46]

A specific method for bismuth was developed by Mahr.[47] Bismuth is precipitated as the complex $Cr(NH_3)_6BiBr_6$, the precipitate is transferred to a distillation apparatus and treated with alkali, and the ammonia is distilled off and titrated. This gives a 2-fold amplification. The bromine amplification cannot be applied in this determination, for the precipitate has to be washed with potassium bromide and so contains excess of it; moreover, bismuth and chromium would be present and might disturb the reaction. Bismuth has also been determined[48] by precipitation as bismuth oxyiodide and then oxidation of the iodide to iodate by chlorine water. The equivalent weight of bismuth when so determined is 34·83.

A better amplification is obtained when bismuth is precipitated as $BiCr(CNS)_6$,[49] and thiocyanate is determined by oxidation with alkaline permanganate.[50] Although 48 equivalents of permanganate are required for only one mole of bismuth, back-titration is necessary, which detracts from the usefulness of the method.

The same compound has been determined by oxidation of the chromium(III) to chromium(VI) with persulphate, followed by iodimetric titration.[51] Reinecke's salt can be determined by a similar process and as this compound is a selective precipitant for mercury and copper, amplification methods for these metals are available.[52] In the presence of thiourea, cadmium can be selectively precipitated and determined likewise.[53]

MISCELLANEOUS DETERMINATIONS

One very old method for the determination of phosphorus gives a remarkable gravimetric amplification. After precipitation of ammonium phosphomolybdate, which in itself does not provide a good weighing form, and its dissolution in ammonia, lead molybdate is precipitated.[54] It can be calculated that the final precipitate is about 140 times the weight of the original amount of phosphorus. This is an excellent method and is hardly to be found in any text-book. Titrimetric methods for phosphorus in which the yellow precipitate is dissolved and the molybdenum is reduced to molybdenum(III) and then titrated,[55] can also be termed indirect amplification methods. Such methods are quite old. More latterly, reduction to molybdenum(V) has been preferred; Birnbaum and Walden[56] dissolved the yellow precipitate, passed the solution through a silver reductor and titrated the molybdenum(V) with cerium(IV) sulphate. The method has been recommended again quite recently.[57] In the latter modification the phosphorus is extracted as phosphomolybdic acid into isobutyl acetate and, after back-extraction, is passed through the silver reductor. It is possible to determine as little as 3 μg of phosphorus with greater precision than by spectrophotometry, for the amplification is 12-fold. In a further method for determination of traces of phosphorus a double amplification is used. Phosphomolybdic acid is extracted into isobutyl acetate and back-extracted into ammonia solution, and molybdate is precipitated as 8-hydroxyquinoline molybdate. The latter is filtered off and the precipitate is dissolved and titrated with standard potassium bromate.

As two moles of 8-hydroxyquinoline are required for one mole of molybdate ions, the final amplification of phosphorus in terms of standard bromate is 96-fold. It is not possible (without great inconvenience) to precipitate 8-hydroxyquinoline molybdate quantitatively when the amount of phosphorus is less than 0·5 μg, otherwise the cerium(IV) perchlorate oxidation (p. 362) could be used and a 720-fold amplification could be exploited. The latter method can, of course, be used provided that precipitation of 8-hydroxyquinoline molybdate is quantitative, but for amounts of phosphorus down to 0·5 μg, the amount of standard bromate is quite measurable and this method is preferred because it is much simpler.[58]

Both phosphorus and silicon have been determined indirectly by atomic absorption spectroscopy after isolation by suitable solvent extraction procedures. The final measurement is again of the molybdenum content of the heteropoly acids.[59]

Colorimetric methods have also been used in which molybdenum is determined spectrophotometrically after precipitation of ammonium phosphomolybdate;[60] in more recent times, phosphomolybdic acid has been extracted and then after back-extraction into an aqueous phase, has been treated with a suitable spectrophotometric reagent for molybdenum.[61] In one recent paper of this kind[62] a new reagent for molybdenum was used.[63] When phosphorus is determined by titration of ammonium phosphomolybdate with alkali the process is one of indirect amplification. The same is true obviously when phosphomolybdate (or silicomolybdate *etc.*) is precipitated with other bases.[64,65]

There are several other miscellaneous reactions which are amplification reactions and which were not so termed in former days. For example, one of the oldest methods for determining sulphate titrimetrically is by treatment of the sulphate solution with barium chromate dissolved in hydrochloric acid.[66] This precipitates barium sulphate and yields an equivalent amount of chromate. The solution is then treated with ammonia to precipitate the dissolved barium chromate and the mixture is filtered off. The filtrate contains chromate equivalent to the original sulphate, and when this is titrated iodimetrically or with standard iron(II) solution it can be seen that an amplification has been achieved.

Several metals which form insoluble iodates have been determined by precipitating them as the iodate and, after dissolution of the precipitate, titrating iodimetrically.

Alternatively, the excess of iodate in the filtrate may be determined. Barium, lead, thorium, mercury and bismuth have been determined in this way.[67]

Carbon dioxide in small amounts has been determined by absorbing it in ammoniacal barium chloride, filtering off the precipitated barium carbonate and then redissolving this in acid and precipitating as barium sulphate.[68] King and Wootton[69] determined carbon dioxide in plasma by absorbing it in barium hydroxide and precipitating the excess of barium ion as iodate; the mixed precipitates were then filtered off, washed, dissolved in acid, treated with potassium iodide and titrated with thiosulphate. It should be noted that this method only amplifies the excess of barium hydroxide. Schöniger[70] has described a method for amplifying carbon dioxide, based on passage over alternate layers of heated carbon and copper oxide

$$CO_2 \xrightarrow{C} 2CO \xrightarrow{O} 2CO_2 \xrightarrow{C} 4CO \textit{ etc.}$$

The amplification can proceed indefinitely and is only limited by the length of the reaction tube.

Traces of hydrogen in steels have been determined by burning to form water, passing the water vapour over calcium carbide to form acetylene, burning the acetylene to carbon dioxide and then measuring this conductimetrically.[71] Theoretically it should be possible to amplify this reaction by passing the water formed from combustion of acetylene through a further layer of calcium carbide to form acetylene again and so on. The yield of carbon dioxide should be doubled with each treatment based on the reaction

$$CaC_2 + H_2O \rightarrow CaO + C_2H_2.$$

Either this reaction is not stoichiometric or there is a combination of this and the other possible reaction

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

for an amount of carbon dioxide less than would be expected is obtained in the second treatment.[72]

The methods proposed recently by Weisz are of interest.[73] In them there is a gradual build-up of precipitate until sufficient is available for measurement by suitable means. For example, if chromate (or silver) is to be determined, first a precipitate of silver chromate is formed. This is then treated with barium chloride.

$$Ag_2CrO_4 + BaCl_2 \rightarrow 2AgCl + BaCrO_4$$

The mixed precipitates are then treated with silver nitrate

$$(AgCl) + BaCrO_4 + 2AgNO_3 \rightarrow Ag_2CrO_4 + Ba(NO_3)_2 + (AgCl).$$

Barium chloride is again added and the process is continued until sufficient precipitate for measurement has been obtained. The process can be automated. Other reactions of a similar nature have been exploited in this way and there are many other possibilities.

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Zusammenfassung—Verstärkungsverfahren wurden schon vor über 100 Jahren verwendet, doch kam der Begriff erst mit der Entwicklung mikroanalytischer Techniken in allgemeinen Gegrauch. In den letzten Jahren entwickelte sich neues Interesse an Verstärkungsverfahren, denn man erkanntem daß man mit ihrer Anwendung in der Spurenanalyse oft ungewöhnlich genaue Ergebnisse erzielen kann. Es wird eine Übersicht über die für verschiedene Kationen und Anionen verfügbaren Verstärkungsverfahren gegeben.

Résumé—Les méthodes d'amplification ont été utilisées pour la première fois il y a de cela plus de 100 ans, mais le terme n'est devenu d'usage général que lors du développement des techniques microanalytiques. Les méthodes d'amplification ont repris de l'intérêt durant les quelques dernières années, car on a réalisé que par leur application à l'analyse de traces il est souvent possible d'obtenir des résultats inhabituellement précis. On passe en revue les méthodes d'amplification disponibles pour divers cations et anions.

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IMPROVED METHOD FOR THE SIMULTANEOUS ABSORPTIOMETRIC DETERMINATION OF COBALT AND NICKEL WITH QUINOXALINE-2,3-DITHIOL

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Summary—A new, more stable reagent, *S*-2-(3-mercaptoquinoxalinyl)-thiuronium chloride (MQT), is proposed for the simultaneous absorptiometric determination of cobalt and nickel. It is hydrolysed rapidly to quinoxaline-2,3-dithiol (QDT) in ammonia buffer at pH 10. In the presence of zinc(II), QDT is stabilized by complex formation and the reagent blanks are reduced. Samples containing cobalt(II) and nickel(II) react with the mixture on warming to give 1:3 cobalt and 1:2 nickel complexes, with maximum absorbances at 472 and 520 mμ respectively. The sensitivity of the method is high, 0·0017 and 0·0028 μg/cm^2 for cobalt and nickel respectively, and there is a significant improvement in accuracy and precision, which is about $\pm 1\%$ over a 15-fold change in cobalt to nickel ratio. The selectivity is moderate; Ag(I), Cu(II), Pd(II), Cd(II), Hg(II), Sn(II), Pb(II), Bi(III) and Pt(IV) cause significant interference but most other common cations and anions can be tolerated.

MANY organic reagents have been proposed for the absorptiometric determination of cobalt and nickel, but relatively few of these are recommended in the standard works[1,2] and many are not available commercially. Some of the more common reagents are shown in Table I, with the sensitivities (μg/cm^2) and approximate selectivities (high, moderate or low) of their reactions with cobalt and nickel. Of these reagents, quinoxaline-2,3-dithiol, (QDT, II), shows considerable promise. Recent papers have recommended its use for the determination of cobalt and nickel[3,4] and platinum and palladium.[5] There are, however, serious disadvantages with quinoxaline-2,3-dithiol in these methods, *viz.*

(*a*) The solid reagent is unstable and requires frequent repurification because the decomposition products interfere with the analytical method.

(*b*) The use of dimethylformamide as solvent is undesirable because it is poisonous and expensive.

(*c*) The solutions of the reagent in dimethylformamide, or other solvents, are very unstable and decompose within a few hours. As the reagent solution is coloured, decomposition causes variation of the high reagent blanks (about 10%) and hence reduces the precision of the methods.

These disadvantages are overcome to a large extent by the use of a new reagent, *S*-2-(3-mercaptoquinoxalinyl)thiuronium chloride, (MQT, I), which is completely stable in the solid state. It is sufficiently soluble and stable in aqueous ethanol for

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TABLE I.—SENSITIVITY AND APPROXIMATE SELECTIVITY OF SOME COMMON ORGANIC REAGENTS FOR COBALT AND NICKEL

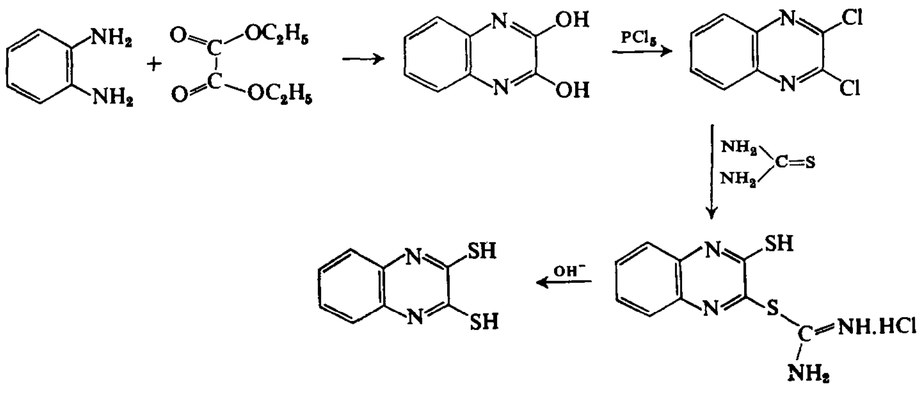
Reagent	Cobalt		Nickel	
	sensitivity, *μg. cm*$^{-2}$	selectivity	sensitivity, *μg. cm*$^{-2}$	selectivity
1-(2-pyridylazo-2-naphthol)	0·0016	high	0·0010	low
quinoxaline-2,3-dithiol	0·0017	moderate	0·0028	moderate
nitroso-R-salt	0·0019	high		
dimethylglyoxime			0·0052	low
2-nitroso-1-naphthol	0·0042	high		
diethyldithiocarbamate			0·010	moderate
thiocyanate	0·055	high		

this to be used as the reagent solution. On addition to an ammonia–ammonium chloride buffer (pH 10) the reagent is immediately hydrolysed to form quinoxaline-2,3-dithiol *in situ*. When zinc ions are incorporated in the buffer solution, the quinoxaline-2,3-dithiol forms a nearly colourless zinc complex which, in addition to stabilizing the reagent solution, will reduce the blank due to excess of quinoxaline-2,3-dithiol in the absorptiometric method. The improved method for the simultaneous absorptiometric determination of cobalt and nickel described here has been based on these observations.

EXPERIMENTAL

Reagents

S-2-(3-Mercaptoquinoxalinyl)thiuronium chloride. The reagent is conveniently prepared in three stages, based on methods given by Newbold and Spring,[6] Stevens *et al.*[7] and Taeger and El-Hawehi.[8] The sequence of reactions is shown below, together with the final hydrolysis of the reagent MQT (I) to form quinoxaline-2,3-dithiol (II). The overall yield of *S*-2-(3-mercaptoquinoxalinyl)thiuronium chloride is about 80% of the theoretical value. It is an odourless, well-crystallized golden-yellow solid, m.p. 273° (decomp.). It can be stored indefinitely without decomposition.



(II) (I)

Elemental analysis of the product recrystallized from absolute ethanol gave C, 39·7%; H, 3·2%; N, 20·4%; S, 23·7%; Cl, 12·9%; $C_9H_8N_4S_2Cl$ requires C, 39·6%; H, 3·33%; N, 20·5%; S, 23·5%; Cl, 13·0%.

The solubility of *S*-2-(3-mercaptoquinoxalinyl)thiuronium chloride in aqueous ethanol at 20° is as follows.

Ethanol, % *v*/*v*	0	20	40	60	80	100
Solubility, *g*/100 *ml*	0·46	0·51	0·83	1·01	0·76	0·34

The reagent is more stable in ethanol-rich solutions, the solution in 80% ethanol being stable for about one week. On decomposition it gives a slight precipitate which can be removed by filtration, the filtrate being used for analysis. The stability of aqueous ethanol solutions is improved by storing them away from light.

An attempt was made to follow the hydrolysis of *S*-2-(3-mercaptoquinoxalinyl)thiuronium chloride spectrophotometrically, as a function of pH and time, but the observations were only semi-quantitative because of decomposition of the quinoxaline-2,3-dithiol formed. The reagent is soluble over the pH range 8–10 and the hydrolysis to quinoxaline-2,3-dithiol is seen as the solutions darken on standing. When zinc ions are added to the reagent in a pH 10 buffer solution there is a marked increase in the stability of the quinoxaline-2,3-dithiol. The hydrolysis of MQT is complete, at pH 10 and in the presence of zinc(II), in less than 5 min. Figure 1, curves A and B, shows the variation of the absorbance of quinoxaline-2,3-dithiol solution as a function of time, at pH 10 in the absence and presence of zinc ions.

S-2-(3-Mercaptoquinoxalinyl)thiuronium chloride solution. A 0·1% w/v solution of the reagent in 80% v/v aqueous ethanol.

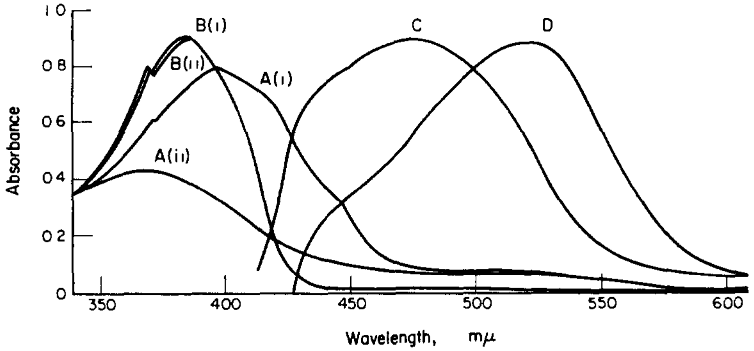


FIG. 1.—Spectra of quinoxaline-2,3-dithiol and its complexes.
Curve *A*—7·3 × 10^{-5} *M* QDT, (*i*) after 15 min and (*ii*) after 1 hr
Curve *B*—the same with excess of zinc(II) present
Curve *C*—1·5 ppm of cobalt(II) with excess of reagent present
Curve *D*—2·5 ppm of nickel(II) with excess of reagent present
All spectra in 8% aqueous ethanol at pH 10

Zinc-buffer solution (pH 10). Dissolve 70 g of ammonium chloride and 6 g of zinc sulphate heptahydrate in 570 ml of ammonia solution (s.g. 0·880) and dilute to 1 litre with distilled water.

Standard solutions of cobalt and nickel for calibration. Prepared from analytical-grade cobalt(II) sulphate heptahydrate and nickel ammonium sulphate.

Apparatus

Measurements of absorbances at fixed wavelengths, for analysis, were made with a Unicam SP 600 spectrophotometer in 1-cm glass cells. Spectral curves were recorded with a Unicam SP 800 instrument.

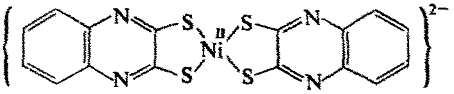
Reaction of reagent with cobalt and nickel

The hydrolysis of *S*-2-(3-mercaptoquinoxalinyl)thiuronium chloride to quinoxaline-2,3-dithiol is best carried out at pH 10, and this fixes the pH of the reaction with nickel and cobalt. No evidence was found for complex formation with the former compound, at this pH. The spectra of the cobalt and nickel complexes of quinoxaline-2,3-dithiol at pH 10 in 8% aqueous ethanol are shown in Fig. 1, curves *C* and *D*. The wavelengths of λ_{max} are 472 and 520 mμ, for the cobalt and nickel complexes respectively. The hypsochromic shift in the spectrum of the quinoxaline-2,3-dithiol in the presence of zinc(II), Fig. 1, curves *A* and *B*, makes a considerable reduction in the absorbance due to excess of reagent at these wavelengths, from about 10% to less than 1% in practice. The molar absorptivities (ε) for the cobalt and nickel complexes on our instrument are

	472 mμ	520 mμ
ε_{Ni}	11,740	20,820
ε_{Co}	35,550	18,110
Ratio $\varepsilon_{Ni}/\varepsilon_{Co}$	0·33	1·15

These values were used to calculate the factors in the simultaneous equations given in the recommended procedure below.

Mole-ratio plots, performed in the usual way,[9] showed that 1:3 cobalt and 1:2 nickel complexes of quinoxaline-2,3-dithiol are the absorbing species in alkaline solution. The rate of formation of the 1:3 cobalt complex is kinetically slow, judged by the rate of development of the maximum absorbance of solutions. This has not been reported by other workers. It was shown that the solution must be heated for 15 min at 60° in ammonia–ammonium chloride buffer in order to establish equilibrium. The presence of oxygen appears to increase the rate. It is possible that the slow rate-determining step is one of oxidation, Co(II)L_2, tetrahedral → Co(III)L_3, octahedral. The 1:2 nickel complex is anionic and was isolated as its di(tetraphenylarsonium) salt. Elemental analysis confirmed the empirical formula of the salt which, since it is diamagnetic (measured at room-temperature only), may have the following square-planar arrangement in the complex anion:



The co-ordination chemistry of this and related complexes of quinoxaline-2,3-dithiol will merit further study.

Of the other variables studied in order to establish the conditions for the method of analysis, it was found that the amount of excess of reagent used was the least critical. About a four-fold molar concentration relative to the metal ion concentration is satisfactory. More critical is the order of the addition of the reagents, which should be first the zinc–buffer solution followed by the MQT in aqueous ethanol, and finally the sample containing cobalt and nickel, in order to minimize errors due to the decomposition of quinoxaline-2,3-dithiol. The ratio of ethanol to water in the final solution is also important because there is a slight bathochromic shift in the λ_{max} of the nickel complex:

Ethanol, % *v*/*v*	10	20	30	40	60	80
λ_{max} (Ni complex), mμ	521	526	529	532	535	537

The cobalt complex is not affected in this way.

Procedure

To 1 ml of the zinc–buffer solution in a 50-ml beaker add 5 ml of the 0·1% reagent solution followed by a suitable aliquot of a sample solution of cobalt(II) and nickel(II) ions (notes 1 and 2). Dilute to 25 ml with water and heat on a steam-bath (60°) for about 15 min. Cool and dilute with water to 50 ml in a graduated flask. Measure the absorbances (*A*) at 472 and 520 mμ in 1-cm cells against the reagent blank prepared in the same way (note 3). Calculate the molar concentrations of cobalt and nickel from the simultaneous equations

$$[\mathrm{Ni}] \times 10^5 = 6{\cdot}74 \times A_{520} - 3{\cdot}43 \times A_{472}$$
$$[\mathrm{Co}] \times 10^5 = 3{\cdot}95 \times A_{472} - 2{\cdot}23 \times A_{520} \text{ (note 4).}$$

Notes

1. The sample is chosen to provide 7·5–75 μg of cobalt and 12·5–125 μg of nickel in the final 50-ml solution.
2. Five ml of 5% aqueous ammonium citrate solution can be added here to suppress the hydrolysis of ions such as Fe(III), Al(III) and Mn(II).
3. The absorbances of the solutions remain constant for several hours.
4. The factors given in the simultaneous equations, calculated from the molar absorptivities measured, will be only approximate for other instruments. The correct factors can be found in the usual way by using standard solutions of cobalt and nickel.

In the determination of cobalt alone, the procedure is the same but the absorbance is measured at 472 mμ only, against a reagent blank. For nickel alone, the heating step can be omitted and the absorbance measured at 520 mμ against a reagent blank. When lower sensitivity is acceptable the isosbestic wavelength at 500 mμ could be used for the determination of total nickel and cobalt.

RESULTS AND DISCUSSION

Beer's law is obeyed in the recommended procedure from 0·15 to 1·5 ppm of cobalt and from 0·25 to 2·5 ppm of nickel. For replicate analyses of cobalt (0·9 ppm) and nickel (1·5 ppm) the overall coefficients of variation were 1·1 and 0·9% respectively. Subtraction of the coefficient of variation for the instrument error, experimental value 0·5%, gave the coefficients of variation for the methodic and operative errors in the procedure as 1·0 and 0·75%, for the determination of cobalt and nickel respectively. Tests were also made of the additivity of the absorbances, for known ratios of cobalt and nickel. The average difference in the absorbances at five different ratios was low—0·01 absorbance units without regard to sign—but the ratio of positive to negative differences was high, 2·9. It is concluded that there is simple additivity of the absorbances and that the recommended procedure is reliable to within ±1%, over a range of cobalt to nickel concentration ratios. The results of analysis of synthetic mixtures of cobalt and nickel, over a 15-fold concentration ratio, which are presented in Table II, confirm this conclusion.

TABLE II.—ANALYSIS OF SYNTHETIC MIXTURES OF COBALT AND NICKEL

Added, *ppm*	Found,* *ppm* Mean	Found,* *ppm* Standard error
Co 0·30 Ni 2·00	0·30 2·04	0·030 0·005
Co 0·30 Ni 1·50	0·31 1·50	0·005 0·018
Co 0·60 Ni 1·00	0·61 1·01	0·005 0·008
Co 0·90 Ni 1·00	0·92 0·98	0·010 0·011
Co 1·20 Ni 0·50	1·19 0·52	0·011 0·007

* Mean and standard error of quintuplicate results.

In the determination of cobalt (0·9 ppm) and nickel (1·5 ppm) the absorbance differed by less than 1% from the expected value in the presence of a 20-fold excess of Na(I), K(I), Ca(I), Mg(II), Zn(II), Al(III), As(V), Ce(IV), Ti(IV), Th(IV), V(V), Cr(VI), Mn(II), Fe(III), Mo(VI), W(VI). To prevent hydrolysis of Fe(III), Mn(II), Al(III), V(V), *etc.*, ammonium citrate must be used as masking agent. Similarly a 200-fold excess of the following anions, present as sodium salts, can be tolerated: F^-, Cl^-, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, citrate and tartrate. There is gross interference by Ag(I), Cu(II), Pd(II), Cd(II), Hg(II), Sn(II), Pb(II), Bi(III) and Pt(IV). The last, as hexachloroplatinate, was found to interfere only with the cobalt determination. These elements must all be removed prior to the determination of cobalt and nickel by the recommended procedure. Since they all form acid-insoluble sulphides it may be possible to precipitate them homogeneously from acid solution by the hydrolysis of thioacetamide[10] with molybdenum as carrier, prior to the absorptiometric determination of the cobalt and nickel.

Acknowledgements—We are indebted to Professor J. F. McGhie for valuable advice on the preparation of the reagent and we acknowledge the grant of part-time study-leave from the Kingston College of Technology to one of us (A. K. S.).

Zusammenfassung—Ein neues stabileres Reagens zur gleichzeitigen absorptiometrischen Bestimmung von Kobalt und Nickel, S-2-(3-Mercaptochinoxalinyl)thiuroniumchlorid (MQT), wird vorgeschlagen. In Ammoniakpuffer bei pH 10 wird es schnell zu Chinoxalin-2,3-dithiol (QDT) hydrolysiert. In Gegenwart von Zink(II) wird QDT durch Komplexbildung stabilisiert und die Blindwerte werden verringert. Kobalt(II) und Nickel(II) enthaltende Proben reagieren mit dem

Gemisch beim Erwärmen zu 1:3-Kobalt- und 1:2-Nickel-Komplexen mit Absorptionsmaxima bei 472 bzw. 520 nm. Die Empfindlichkeit der Methode ist hoch, 0,0017 und 0,0029 $\mu g/cm^2$ für Kobalt bzw. Nickel; Genauigkeit und Richtigkeit steigen beträchtlich an auf etwa ±1% bei einer 15-fachen Ånderung des Kobalt:Nickel-Verhältnisses. Die Selektivität ist mäßig: Ag(I), Cu(II), Pd(II), Cd(II), Hg(II), Sn(II), Pb(II), Bi(III) und Pt(IV) stören beträchtlich, die meisten anderen häufig vorkommenden Kationen und Anionen dürfen dagegen anwesend sein.

Résumé—On propose un nouveau réactif, plus stable, le chlorure de S-2-(3-mercaptoquinoxalinyl)thiouronium (MQT) pour la détermination absorptiométrique simultanée du cobalt et du nickel. Il est rapidement hydrolysé en quinoxaline 2,3-dithiol (QDT) en tampon ammoniaque à pH 10. En la présence de zinc(II), le QDT est stabilisé par formation de complexe et les témoins du réactif sont diminués. Les échantillons contenant le cobalt(II) et le nickel(II) réagissent avec le mélange par chauffage pour donner les complexes 1:3 cobalt et 1:2 nickel avec maximums d'absorption à 472 et 520 mμ respectivmment. La sensibilité de la méthode est élevée, 0,0017 et 0,0029 $\mu g/cm^2$ pour le cobalt et le nickel respectivement, et il y a une amélioration importante en justesse et précision, qui est d'environ ±1% tandis que le rapport du cobalt au nickel varie de 1 à 15. La sélectivité est modérée; Ag(I), Cu(II), Pd(II), Cd(II), Hg(II), Sn(II), Pb(II), Bi(III) et Pt(IV) causent une gêne importante mais la plupart des autres cations et anions communs peuvent être tolérés.

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MASS SPECTROMETRY OF METAL CHELATES—III*

FURTHER STUDIES ON METAL OXINATES

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Summary—The mass spectra of the oxinates of gallium, dysprosium, beryllium, samarium, cadmium, neodymium, indium, bismuth, lanthanum, yttrium and gadolinium have been recorded. The results have been correlated with the structures proposed in the literature. The integrated ion current method has been applied to determine submicrogram quantities of some of these compounds. Oxinates insoluble in organic solvents or undergoing reaction on solution were precipitated directly in the evaporation probe. The factors which determine the suitability of metal chelates for the estimation of metals by this method are discussed together with the instrumental factors which determine the ultimate sensitivity.

IN A previous paper of this series[1] the possibility of estimating very small quantities of volatile metal chelates by integrating the ion current at a significant *m/e* value while evaporating the metal chelate directly into the ion source of a mass spectrometer was demonstrated. Amounts of the order of 10^{-12} g of nickel dimethylglyoximate could be estimated in this way and the method was completely specific. The method was extended later[2] to the oxinates of common metals when it was found that there was a considerable difference in the sensitivity of the method for different metals. It was also discovered that some metal oxinates undergo thermal decomposition to provide products of which the mass spectra contain peaks corresponding to ions containing more than one metal atom. Because of the insolubility of some metal oxinates it was impossible to calibrate the instrument by using successive dilutions of a standard solution of the metal oxinate in an organic solvent. It is the purpose of the present paper to describe an alternative method by which the instrument may be calibrated for such insoluble metal chelates and to outline a variation of the original method by which it is no longer necessary to make any measurements of the pressure of the calibrating gas. It is a further object to extend the method to a number of other metal oxinates and to record their mass spectra in order to correlate them with the proposed structures described in the literature. Finally the experimental parameters which determine the ultimate instrumental sensitivity for the integrated ion current method are examined.

EXPERIMENTAL

All measurements were carried out with an A.E.I. M.S.9 mass spectrometer. The oxinates of gallium, dysprosium, beryllium, samarium, cadmium, neodymium, indium, lanthanum, yttrium and gadolinium were prepared by methods described in the book "Oxine and its Derivatives".[3] A 0·01% solution of gallium oxinate was prepared by dissolving 1 mg in 10 ml of chloroform.

The oxinates of cobalt, nickel, iron(III), manganese, beryllium, cadmium, indium and samarium

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* Part II—Talanta, 1967, **14**, 1213.

were precipitated directly in pyrex glass tubes 27-mm long and 1-mm internal diam. which were fitted into the direct insertion probe and discarded after use. The precipitation was achieved by injecting 1 μl of the metal salt solution into the tube followed by 1 μl of a 2% solution of oxine in ethanol and 1 μl of $4M$ ammonia. Heptacosafluoro-tri-n-butylamine was supplied by Koch-Light Laboratories Ltd. The procedure for recording the integrated ion current was that described previously.[1] A method which eliminates the need for an accurate measurement of the pressure of heptacosafluoro-tri-n-butylamine in the inlet system or source of the mass spectrometer involves the evaporation of a standard sample of known weight of the metal chelate while a constant appropriate but unknown pressure of the calibrating gas is maintained in the source. All subsequent unknown samples of the same metal chelate are then evaporated under the same conditions.

The concentration of unknown and standard samples may then be compared directly, the peak heights due to the calibrating gas giving an indication of any variation in instrumental sensitivity between or during measurements.

RESULTS AND DISCUSSION

The calibration of a mass spectrometer for the measurement of small concentrations of metal chelates by the integrated ion current method presents a severe problem in that it is impossible to handle weighed submicrogram quantities. The only alternative is to measure by volume samples of solutions which have been successively diluted from an original solution. In the previous paper of this series[2] it was found that such a calibration could not be made for the oxinates of cobalt, nickel, iron(III) and manganese because these compounds were not sufficiently soluble in chloroform or dioxan to provide even a 0·01 % solution. These compounds were soluble in dimethylformamide but when samples of the solution were evaporated into the source of the mass spectrometer the mass spectra recorded did not reveal peaks due to ions containing metal atoms. A similar effect was observed when cadmium oxinate was dissolved in dimethyl sulphoxide. It is probable that dissociation of the metal complex takes place in these polar solvents. The decomposition of nickel dimethylglyoximate in chloroform solution has been reported previously[1] and the dissociation of metal chelates in solvents of this type is the subject of a further communication.

In order to avoid the difficulty of calibration with insoluble compounds it was decided to precipitate the metal oxinates from small measured volumes of standard solutions of the metal salts directly in the evaporation tube by the addition of an excess of an ammoniacal solution of oxine in aqueous ethanol. The solvent and ammonia are evaporated immediately during the introduction of the sample and the presence of excess of oxine in the residual solid material was considered to be unimportant.

Transition metal oxinates

When solutions of iron(III), cobalt, nickel and manganese were mixed with the oxine solution in the evaporation tube the metal oxinate could be seen to precipitate, and on evaporation of the product into the source of the mass spectrometer, integrated ion current curves could be obtained at significant m/e values. Nevertheless the sensitivity obtained by this method was lower than that observed previously and this could be due either to incomplete precipitation or to decomposition during evaporation. In order to compare the sensitivities for different metal chelates or for different chelates of the same metal or for different methods of sample introduction it is necessary to introduce a standard sensitivity figure. This cannot be regarded as having an absolute and constant value but rather a relative value since all the sensitivities will vary with instrumental parameters in the manner discussed later. The arbitrary definition chosen for the sensitivity value is the area under the ion current curve at a significant m/e value, in mm^2, divided by the sample weight in g and multiplied by 10^{-12}. In these preliminary studies the sensitivity (s) is measured at low electron multiplier gain, using the least sensitive galvonometer recorder trace, a slow recorder paper speed and a filament emission of 100 μA; an increase of several orders of magnitude in sensitivity is possible by adjustment of these instrumental parameters.

Iron(III) oxinate. The metal chelate was precipitated in the evaporation tube from a 0·1% solution of iron(III) chloride. Evaporation took place at 390° and the integrated ion current sensitivity at $m/e = 344$ was $s_{344} = 2{\cdot}0 \times 10^{-4}$. This means that the limit of detection at low sensitivity lies between 10^{-8} and 10^{-9} g.

Cobalt(II) oxinate. Precipitation of the metal chelate took place from 1 μl of a 0·1% solution of cobalt nitrate. Evaporation took place at 400° and the sensitivity at $m/e = 347$ [corresponding to the ion $Co(Ox)_2^+$] was $s_{347} = 2{\cdot}0 \times 10^{-4}$.

Manganese(II) oxinate. Precipitation occurred from 1 μl of a 0·1% solution of manganese(II) sulphate. Evaporation took place at 390° and the sensitivity at $m/e = 343$ [corresponding to the ion $Mn(Ox)_2^+$] was $s_{343} = 7{\cdot}0 \times 10^{-4}$.

Nickel oxinate. Precipitation occurred from 1 μl of a 0·1% solution of nickel sulphate. Evaporation took place at 400° and the sensitivity at $m/e = 346$ [corresponding to the ion $Ni(Ox)_2^+$] was $s_{346} = 3{\cdot}0 \times 10^{-4}$.

Gallium oxinate

Gallium oxinate is soluble in chloroform and a 0·01% solution was prepared. The mass spectrum of gallium oxinate was recorded at an evaporation temperature of 320° and was in accordance with the structure $Ga(Ox)_3^+$, exhibiting intense peaks at $m/e = 501$ [$Ga(Ox)_3^+$], 357 [$Ga(Ox)_2^+$] and 213 [$Ga(Ox)^+$]. The peak at $m/e = 357$ was chosen for an integrated ion current measurement as it was close to a convenient peak from the calibrating gas. The sensitivity was $s_{357} = 2{\cdot}25 \times 10^{-3}$.

Indium oxinate

Indium oxinate is not soluble in an inert organic solvent and it was precipitated directly in the evaporation tube from 1 μl of 0·1*M* indium chloride. Evaporation took place at 395° and the mass spectrum was in accordance with the structure $In(Ox)_3^+$, exhibiting strong peaks at $m/e = 547$ [$^{115}In(Ox)_3^+$], 403 [$^{115}In(Ox)_2^+$] and 259 [$^{115}In(Ox)^+$]. The sensitivity was $s_{403} = 3{\cdot}2 \times 10^{-5}$. Although there is no sign of decomposition, this sensitivity is very low and suggests incomplete precipitation of indium oxinate.

Beryllium oxinate

The structure of beryllium oxinate has been the subject of considerable discussion and the most recent paper[4] proposes the structure $Be_2O.Ox_2.2H_2O$ on the basis of evidence derived from infrared absorption and differential thermal analysis. At temperatures between 180 and 270° one molecule of water is lost and at higher temperatures hydrolysis takes place with the loss of oxine and the final formation of beryllium oxide. Evaporation into the source took place at 380° and the mass spectrum showed intense peaks at $m/e = 296$ [$Be(Ox)_2^+$] and 153 [$Be(Ox)^+$]. However, it is known that the mode of decomposition of oxinates may vary with the conditions, so the two results are not necessarily in conflict. There is also evidence of polymerization provided by the appearance of a peak at $m/e = 450$, corresponding to the ion $Be_2(Ox)_3^+$. The sensitivity is very low; $s_{297} = 4{\cdot}0 \times 10^{-4}$.

Cadmium oxinate

Cadmium oxinate is insoluble in chloroform and undergoes decomposition when dissolved in dimethyl sulphoxide. It was therefore precipitated directly from 1 μl of 0·1*M* cadmium sulphate. Evaporation took place at 365°, and the mass spectrum revealed small peaks at $m/e = 500$ [$^{106}Cd_2(Ox)_2^+$] in addition to larger peaks at $m/e = 394$ [$^{106}Cd(Ox)_2^+$] and 252 [$^{106}Cd(Ox)^+$]. There are thus signs of thermal decomposition and polymerization. The sensitivity, $s_{394} = 1{\cdot}6 \times 10^{-5}$, was correspondingly low.

Bismuth oxinate

Solid bismuth oxinate could be evaporated at a temperature of 390° but the highest peak in the mass spectrum was at $m/e = 497$, corresponding to the ion $Bi(Ox)_2^+$. However, it is insoluble in suitable organic solvents, and when precipitated directly from bismuth nitrate solution the sample charred on heating and did not give a reproducible mass spectrum.

Rare earth oxinates

Samarium oxinate was insoluble in inert organic solvents and was precipitated directly from 1 μl of 0·1*M* samarium chloride. Evaporation took place at 395° and the mass spectrum was in accordance with the structure $Sm(Ox)_3$, exhibiting peaks at $m/e = 584$ [$^{152}Sm(Ox)_3^+$], 440 [$^{152}Sm(Ox)_2^+$] and 296 [$^{152}Sm(Ox)^+$]. The sensitivity was $s_{440} = 4{\cdot}0 \times 10^{-5}$.

Neodymium oxinate. There has been some difference of opinion about the existence of neodymium oxinate of constant composition although samples corresponding to the formula $Nd(Ox)_3$ have been prepared. The complex was not considered stable, and so the mass spectrum is of particular interest. Evaporation into the source occurred at a temperature of 400°, and the mass spectrum was very complex. Among the mass peaks which could be identified were those at $m/e = 286$ [$Nd(Ox)^+$], 430 [$Nd(Ox)_2^+$], 574 [$Nd(Ox)_3^+$] and 716 [$Nd_2(Ox)_3^+$], but there are also peaks between 800 and 1050 which could not be positively identified without mass measurement but are probably due to $Nd_3(Ox)_3^+$, $Nd_3(Ox)_4^+$ and $Nd_4(Ox)_4^+$. It is not possible to say with certainty whether these peaks are due to thermal polymerization at a temperature of 400° or whether the sample contains polymer.

A similar spectrum is obtained with dysprosium oxinate. Gadolinium oxinate on the other hand provides a simple mass spectrum agreeing with the structure $Gd(Ox)_3$ and exhibiting peaks at $m/e = 588$ [$^{156}Gd(Ox)_3^+$] and 444 [$^{156}Gd(Ox)_2^+$]. Evaporation took place at a temperature of 395° from a sample precipitated directly in the evaporation tube by mixing 1 μl of 0·1*M* gadolinium chloride with 1 μl of a 2% solution of oxine in ethanol and 1 μl of 4*M* ammonia. The sensitivity $s_{444} = 4{\cdot}0 \times 10^{-5}$ was low owing to the fact that only one isotopic species was being measured.

When solid lanthanum oxinate was evaporated into the source at a temperature of

415° the highest mass peak recorded in the spectrum was at *m/e* = 427. This corresponds to the ion $La(Ox)_2^+$ but this peak could not be used with the integrated ion current method because the reference compound provides a mass spectrum with a peak at the same *m/e* value.

A sample of yttrium oxinate charred on heating to 410° and the mass spectrum was found to be very complex. In addition to the molecule ion at *m/e* = 521 there were peaks at higher *m/e* values up to 1500. This behaviour may be due to thermal polymerization although it has been reported previously that the complex is not stoichiometric.

Factors influencing instrumental sensitivity

The sensitivity of the integrated ion current method is dependent on two groups of variables, the first group being associated with the sample and the second with the instrument.

Sample factors. The most important sample characteristic determining sensitivity is the sublimation temperature. The method relies on the identification of a moderately sharp rise and fall in the ion current at a selected *m/e* value when the sample is lowered into the heating region of the source. If the rate of evaporation is too slow, the individual peak heights will be small and separation from the background difficult, even though the total integrated ion current as represented by the total area under the peaks would still be significant. The measurement of broad low peaks in gas chromatography presents a similar problem. Secondly the sample may decompose on evaporation, either dissociating or polymerizing so that the intensity at any selected *m/e* value will be lower. Then even if the sample does not decompose it may not always be possible to use the most intense mass peak because of superposition of reference compound peaks or the unavailability of a suitable adjacent reference compound peak. It may thus be necessary to use a sample peak of low intensity with corresponding loss in sensitivity. There are two factors which may alter sensitivity and therefore reproducibility. It is possible that evaporation of a minor component from a mixture may be affected by the nature or state of the matrix. In the absence of such a matrix it is still possible that the disposition of the sample within the evaporation tube may affect the transient change in source pressure and hence the sensitivity. Neither effect has been identified in practice. Finally the metal may have a number of isotopes of equal abundance so that the ion current for any specific ionization process is distributed over a number of *m/e* values with corresponding loss of sensitivity since only one of the isotopes will be involved. A specific example is that of gadolinium oxinate which has low sensitivity for this reason.

Instrumental factors. The A.E.I. M.S.9. read-out is on a Honeywell Brown U.V. Recorder which provides a number of simultaneous records at different degrees of attenuation. All sensitivities quoted are based upon the least sensitive record, at least two orders of magnitude increase in sensitivity being obtainable by using the most sensitive record. Because of the problem of calibrating the instrument at the higher sensitivity, measurements are first made at low sensitivity. A second factor controlling instrumental sensitivity is the electron multiplier gain which is determined by the voltage applied to the dynodes. The gain is normally low because of calibration difficulties when the instrument is operated at high gain, but a further hundredfold increase in sensitivity may be obtained by increasing the electron multiplier gain.

The limitation here is the random noise in the instrument. A further increase in sensitivity (by a factor of only 3) is possible if the electron beam current is increased from the conventional 100 μA to 500 μA. Finally there is an apparent gain in sensitivity if the recorder paper speed is increased, as the area of the peak is then greater. However this is not a real gain permitting lower levels of sample size to be measured, because the peak height is not increased. At low levels the discrimination against noise is given by the peak height and not the peak area.

We can now make some general observations about the sensitivity for various metal chelates. In the case of the first compound studied with this technique, nickel dimethylglyoximate, the sensitivity $s_{288} = 1{\cdot}07 \times 10^{-3}$ was high and when the instrument was adjusted for maximum performance the sample size could be lowered to 10^{-12} g for measurements and 10^{-14} g for detection. This sensitivity can be compared with that obtained for an average organic compound of appropriate volatility, *p*-hydroxyphenylethylamine, for the base peak of which $s_{107} = 1{\cdot}15 \times 10^{-3}$. The sensitivities for all the metal oxinates studied in this paper are lower than these values so that from the point of view of this method of determination oxine may not be as satisfactory as other chelating agents.

Zusammenfassung—Die Massenspektren der Oximate von Gallium, Dysprosium, Beryllium, Samarium, Cadmium, Neodym, Indium, Wismut, Lanthan, Yttrium und Gadolinium wurden registriert. Die Ergebnisse wurden mit den in der Literatur vorgeschlagenen Strukturen in Beziehung gesetzt. Zur Bestimmung von Submikrogrammengen einiger dieser Verbindungen wurde die Methode des integrierten Ionenstroms angewandt. In organischen Lösungsmitteln unlösliche Oximate und solche, die beim Lösen Reaktionen eingehen, wurden direkt in der Verdampfungskammer gefällt. Es werden die Faktoren diskutiert, die die Eignung von Metallchelaten zur Bestimmung von Metallen nach dieser Methode bedingen, sowie die die Empfindlichkeitsgrenze bestimmenden instrumentellen Einflüsse.

Résumé—On a enregistré les spectres de masse des oxinates de gallium, dysprosium, béryllium, samarium, cadmium, néodyme, indium, bismuth, lanthane, yttrium et gadolonium. Les résultats ont été reliés aux structures proposées dans la littérature. On a appliqué la méthode du courant d'ion intégré pour déterminer des quantités à l'échelle du submicrogramme de quelques-uns de ces composés. Les oxinates insolubles en solvants organiques ou subissant une réaction en solution ont été précipités directement dans l'éprouvette d'évaporation. On discute des facteurs qui déterminent l'intérêt des chélates métalliques pour le dosage des métaux par cette méthode en même temps que des facteurs instrumentaux qui déterminent la sensibilité finale.

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ZUR POLAROGRAPHIE DER n-BUTYLZINNCHLORIDE

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Zusammenfassung—Di-n-butylzinndichlorid (II) und Tri-n-butylzinnchlorid (III) lassen sich neben Mono-n-butylzinntrichlorid (I) bei Anwesenheit von Diphenyldithiocarbamat gleichstrompolarographisch bestimmen. Die Untersuchungen werden in einer 5-%igen Natriumacetattrihydrat-Methanollösung durchgeführt, um die offensichtlich zwischen II bzw. III und Diphenyldithiocarbamat gebildeten, polarographisch aktivem "Dithiocarbamate" zu lösen und um I als Acetat zu maskieren. In gewissen Grenzen besteht Proportionalität zwischen Wellenhöhe und Konzentration. In einem Organozinnchloridgemisch wird der Gehalt an I komplexometrisch ermittelt. Tetra-n-butylzinn ist in Methanol nahezu unlöslich und stört die Bestimmungen nicht.

Mono-n-butylzinntrichlorid (I), Di-n-butylzinnchlorid (II), Tri-n-butylzinnchlorid (III) und Tetra-n-butylzinn (IV) lassen sich bekanntlich gravimetrisch, gaschromatographisch,[1–3] oszillopolarographisch[4] oder mit Hilfe der Gleich- bzw. Wechselstrompolarographie[5–10] quantitativ bestimmen. Versuche einer quantitativen Ermittlung von I–IV nebeneinander verliefen ergebnislos. So führte die Gleichstrompolarographie weder zu gut ausgebildeten Grenzströmen noch zu auswertbaren Polarogrammen. Die hier durch I verursachten hohen Maxima überdecken die Stufen von II und III.[8–10] Auch oszillopolarographisch waren maximal nur zwei Komponenten, wenn die Konzentration einer dritten konstant gehalten wurde, nebeneinander zu bestimmen.[4] Nach allem scheint eine polarographische Analytik von I–III nebeneinander nur dann möglich zu sein, wenn eine der Komponenten durch Zugabe geeigneter Salze oder Komplexbildner stabilisiert bzw. komplexgebunden wird, was eine Trennung der polarographischen Stufen zur Folge haben würde.

Im Zusammenhang polarographischer Untersuchungen verschiedener substituierter Organozinn-dithiophosphinate bzw. -dithiophosphorsäureester[11] waren gut ausgeprägte und in nichtwäßrigen Solventien charakteristische polarographische Stufen zu beobachten. Schwefelhaltige Komplexliganden wie Thiocarbonsäuren, Dithiophosphinsäuren, Dithiocarbonate u.a. liefern in wäßriger Lösung mit Organozinnhalogeniden, hier vor allem I und II, offensichtlich unter Abspaltung von Halogenwasserstoff, die entsprechenden Reaktionsprodukte. Diese sind in Wasser unlöslich, gut filtrierbar und teilweise zur selektiven Abtrennung verschiedener Organozinnhalogenide geeignet. In Methanollösungen, die Natriumacetat und Diphenyldithiocarbamat enthalten, ist eine gleichzeitige gleichstrompolarographische Bestimmung von II und III neben I möglich. Natriumacetat verhindert, daß I die Elektrodenvorgänge von II und III beeinflußt. Gut auswertbare polarographische Stufen wurden hier aber nur unter Verwendung einer gesättigten Kalomelelektrode als Gegenelektrode erhalten.

Versuche, mit Bodenquecksilber als Gegenelektrode[4,9,10] führten zu negativen Ergebnissen.

Im folgenden soll zunächst ausschließlich über die polarographische Bestimmung von I–III berichtet werden. Eine Diskussion über den Mechanismus dieser elektrochemischen Reaktion ist für spätere Arbeiten vorgesehen.

EXPERIMENTELLER TEIL

Die polarographischen Untersuchungen werden mit dem Gleichstrompolarographen PTS 4 im Potentialbereich von —0,6 bis —1,6 V—Dämpfung 3, Empfindlichkeit 5 μA—durchgeführt. Als Gegenelektrode dient eine gesättigte Kalomelelektrode (SCE). Die Tropfzeit der Kapillare beträgt bei einer Behälterhöhe von 63 cm 5,2 sec/Tropfen. Als Grundelektrolyt wird eine 5-%ige Lösung von Natriumacetattrihydrat *p.A.* in Methanol *p.A.* verwendet. Als Komplexbilder für die Butylzinnchloride dient eine 0,4-%ige methanolische Diphenyldithiocarbamatlösung. Das hierfür verwendete Diphenyldithiocarbamat wird nach bekanntem Verfahren[16] hergestellt. Die Untersuchungen werden in einem Kalousekgefäß durchgeführt. Vor der polarographischen Untersuchung wird die Meßzelle mehrmals mit Argon sekuriert und dann unter Inertgasatmosphäre Grundelektrolyt, jeweilige Substanzprobe und Komplexbildnerlösung zugegeben.

1. *Bestimmung von Monobutylzinntrichlorid,(I), mit Komplexon III*[4,12]

Zehn ml einer sauren alkalischen oder alkoholischen Lösung, die I enthält, werden mit 30 ml Eisessig und 3 Tropfen einer 0,1-%igen wässrigen Brenzkatechinviolettlösung versetzt. Bis zum Farbumschlag von Rot nach Blau wird festes Natriumacetat zugegeben. Ein Überschuß an Natriumacetat gestaltet den Titrationsverlauf günstig. Zu dieser Lösung läßt man eine 0,1 bis 0,01m Lösung von Komplexon III bis zum Farbumschlag von Blau nach Gelbrosa tropfen. Kurz vor Erreichen des Äquivalenzpunktes ist es erforderlich, nach Zugabe jedes Tropfens der Komplexonlösung zu rühren oder zu schütteln. Während der Titration ist auf Temperaturkonstanz (nicht über 20°) zu achten.

1 ml einer 0,1m Komplexonlösung = 28,22 mg Butylzinntrichlorid.

2. *Bestimmung von Dibutylzinndichlorid,(II), neben Butylzinntrichlorid,(I), unter Verwendung von Thioglykolsäure*

Ein ml einer Petrolätherlösung von I und II wird mit 10 ml Petroläther (Sdp. 50–60°) und 0,2 ml Thioglykolsäure versetzt. Nach Zugabe von 5–10 ml Wasser fällt das Dibutylzinnthioglykolat aus. Diese wird nach 3 std. Stehen abfiltriert, mit wenig Wasser gewaschen und in 5 ml Äther und Methanol quantitativ gelöst. Für das Auflösen des Niederschlages ist es günstig, ein 25 ml Meßkölbchen zu verwenden. Der Meßkolben wird mit Grundelektrolyt (1-%ige methanolischer Lithiumchloridlösung) aufgefüllt und diese Lösung in einem Kalousekgefäß polarographiert. Das Kalousekgefäß wird auf 25 ml geeicht, um den während des Sekurierens verdunsteten Petroläther durch Grundelektrolyt zu ergänzen. Enthält die bekannte Substanzprobe 0–20% Dibutylzinndichlorid so ist eine Einwaage von 1 g Substanzgemisch auf 100 ml Petroläther (Sdp.50–60°) zu empfehlen. Von dieser Lösung wird 1 ml, wie beschrieben, für die polarographische Untersuchung verwendet. Im Falle einer geringeren Konzentration an II werden 2–5 ml der Petrolätherlösung eingesetzt.

3. *Bestimmung von Dibutylzinndichlorid, (II), neben Monobutylzinntrichlorid, (I), unter Verwendung von Diphenyldithocarbomat*

Ein Substanzgemisch bekannter Zusammensetzung von II und I (vgl. Eichkurve) wird in einem Kalousekgefäß mit Grundelektrolytlösung (5-%ige methanolische Natriumacetattrihydratlösung) bis auf 25 ml aufgefüllt. Nach Sekurieren mit Argon werden 2 ml einer 0,4-%-igen methanolischen Diphenyldithiocarbamatlösung zugegeben. Die Reihenfolge dieser Operation ist unbedingt einzuhalten, um eine Umsetzung von I in das entsprechende Acetat zu gewährleisten und um eine vorzeitige Komplexbildung zu vermeiden; andernfalls sind die polarographischen Stufen nicht zu trennen. Für die Herstellung des Grundelektrolyten ist nur Natriumacetattrihydrat geeignet, da die Verwendung wasserfreien Natriumacetats nicht auswertbare Polarogramme liefert. Die Polarographie wird in einem Potentialbereich von —0,6 bis —1,4 V und mit einer Empfindlichkeit von 2 μA durchgeführt.

Erfassungsgrenze: 0,0037–0,148 mg/ml II neben 0–0,37 mg/ml I mit einer Genauigkeit ±3%.

4. *Bestimmung von Dibutylzinndichlorid (II) und Tributylzinnchlorid (III) nebeneinander*

Wie unter 3. beschrieben, wird ein bekanntes Substanzgemisch von II und III (vgl. Eichkurve) in 25 ml 5-%iger methanolischer Natriumacetattrihydratlösung gelöst und mit 1 ml einer 0,4-proz.

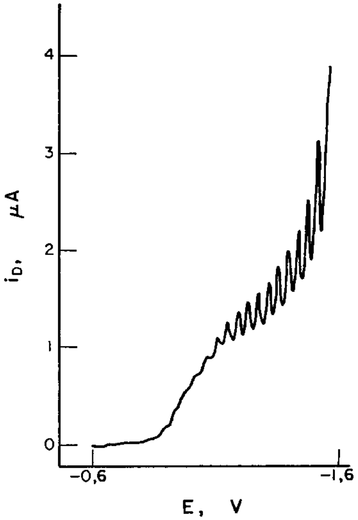

ABB. 1.—Polarographische Stufen von $(C_4H_9)_2SnCl_2$, 2,6 mg in 25 ml 1-%iger Lithiumchlorid Methanollösung, Empfindlichkeit 5 μA.

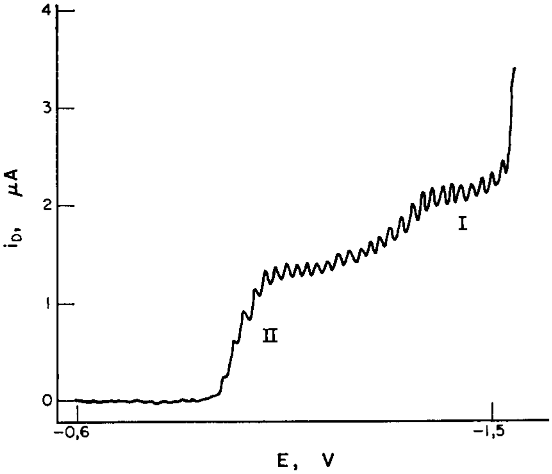

ABB. 2.—Polarographische Stufen von $(C_4H_9)_2SnCl_2$ (II) (3,45 mg) in Gegenwart von $C_4H_9SnCl_3$ (I) (4,01 mg) in 25 ml 5-%iger Natriumacetat Methanollösung nach Zugabe von 2 ml 0,4-%iger Natriumdiphenyldithiocarbamatlösung.

methanolischer Diphenyldithiocarbamatlösung versetzt. Das Reaktionsgemisch wird nach üblicher Verarbeitung in einem Potentialbereich von −0,6 bis −1,6 V bei einer Empfindlichkeit von 5 μA polarographiert. Die Empfindlichkeitsgrenze beträgt 0,00384–0,308 mg/ml III und 0,00384–0,154 mg/ml II mit einer Genauigkeit von ±3%. Als Grundelektrolyt für diese Untersuchungen ist auch 1-%ige methanolischer Lithiumchloridlösung verwendbar.

5. *Bestimmung von Dibutylzinndichlorid, (II), Tributylzinnchlorid, (III), und Butylzinntrichlorid*

Eine Substanzprobe von I, II und III (vgl. Eichkurve) wird wie üblich in einem Kalousekgefäß in 5%iger methanolischer Natriumacetattrihydratlösung gelöst und auf 25 ml aufgefüllt. Danach gibt man 1 ml einer 0,4-%ige Methanollösung von Diphenyldithiocarbamat zu und polarographiert in einem Potentialbereich von −0,6 bis −1,6 V bei einer Empfindlichkeit von 5 μA. Der Gehalt an I wird analog 1. ermittelt.

Erfassungsgrenze: 0,2 bis 4 mg (0,00768–0,154 mg/ml) II, 0,2 bis 8 mg (0,00786–0,308 mg/ml) III neben 4 mg (0,154 mg/ml) I in je 26 ml Lösung.

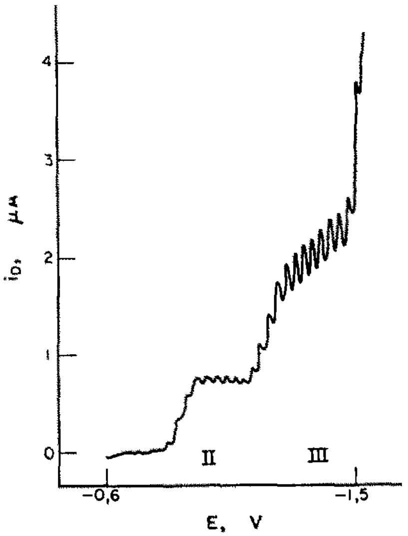

Abb. 3.—Polarographische Stufen von $(C_4H_9)_2SnCl_2$ (II) (1,95 mg) und $(C_4H_9)_3SnCl$ (III) (5,85 mg) in 25 ml 5-%iger Natriumacetat Methanollösung nach Zugabe von 1 ml 0,4-%iger Natriumdiphenyldithocarbamatlösung.

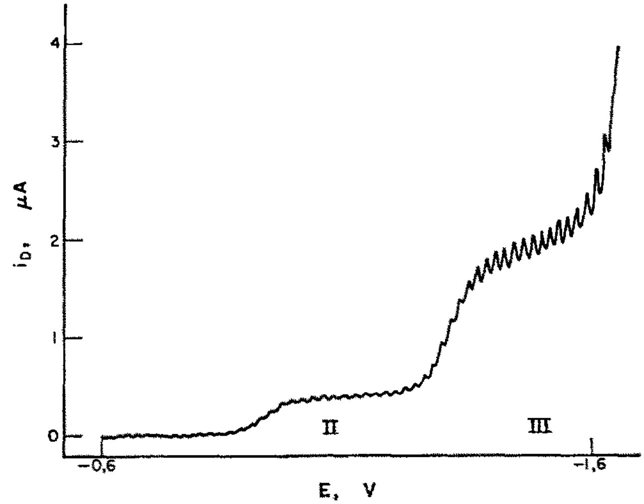

Abb. 4.—Polarographische Stufen von $(C_4H_9)_2SnCl_2$ (II) (0,59 mg) und $(C_4H_9)_3SnCl$ (III) (6,66 mg) neben $C_4H_9SnCl_3$(I) (2,00 mg) in 25 ml 5% iger Natriumacetat Methanollösung nach Zugabe von 1 ml 0,4-% iger Natriumdiphenyldithiocarbamatlösung.

DISKUSSION DER ERGEBNISSE

Aus einer Mischung von Mono-n-butylzinntrichlorid (I) und Di-n-butylzinndichlorid (II) in Wasser wird nach Zugabe von Thioglykolsäure und Petroläther II als Thioglykolat ausgefällt. Der Niederschlag wird nach quantitativer Filtration und Lösen in Methanol/Äther nach Zugabe von Lithiumchlorid als Leitsalz polarographiert.

Man erhält für II eine gut auswertbare Stufe mit dem Halbstufenpotential $E_{1/2} = -0{,}924$ V gegen SCE. Zwischen der Stufenhöhe und der Konzentration im Bereich von 0 bis 2,77 mg II/25 ml Lösung besteht Proportionalität.

Im Falle höherer Konzentrationen von II erfolgt starke Adsorption an der Quecksilberoberfläche, es besteht also hier keine Proportionalität zwischen der Wellenhöhe und der Konzentration des Depolarisators.

Das Filtrat der Mischung enthält I als Hydrolysat, das in zwei Stufen an der Quecksilbertropfelektrode reduziert wird. Es sind zwei gut ausgeprägte Wellen zu beobachten, deren erste der Konzentration von I proportional ist. Obwohl sich der Gehalt von I einer Lösung auf diese Weise ermitteln läßt, ist es vorteilhafter, I neben II komplexometrisch mit Komplexon III quantitativ zu bestimmen.[4,12,13] Störungen für diese Titration treten durch zu geringe Eisessigkonzentration—sie sollte 60% betragen—und durch Zinn(IV)-ionen, die hier miterfaßt werden, auf. Die Erfassungsgrenze dieser Methode erlaubt, 6 mg I neben 2 g II quantitativ nachzuweisen.

Weit günstiger verläuft die gleichstrompolarographische Bestimmung von II in einem Gemisch mit I unter Verwendung von Diphenyldithiocarbamat statt Thioglykolsäure und bei Anwesenheit von Natriumacetat. Letzteres führt das leicht hydrolysierbare I in das stabilere Acetat[14] über, was eine Verschiebung des Halbstufenpotentials von I zu negativeren Potentialen zur Folge hat. II reagiert mit Natriumdiphenyldithiocarbamat unter Komplexbildung vermutlich zu dem entsprechenden Dithiocarbamat, dessen polarographische Stufe sich nun deutlich von der des Mono-n-butylzinntrichlorids unterscheidet (vgl. Abb. 2). Die Gehaltsermittlung von I wird auch hier durch komplexometrische Titration vorgenommen.[13] Nach dieser Methode waren 0,1 bis 4 mg II in 27 ml neben 0 bis 10 mg I in 27 ml mit einer Genauigkeit von ±3% nachzuweisen.

Auch II und Tri-n-butylzinnchlorid (III) lassen sich in 5-%iger methanolischer Natriumacetatlösung als Grundelektrolyt nach Zugabe von Diphenyldithiocarbamat im gewissen Konzentrationsbereich leicht polarographisch nebeneinander bestimmen.

Bei gleicher Konzentration verhalten sich die Höhen der polarographischen Stufen von II und III wie 2:1 (vgl. Abb. 3). In den Grenzen von 0,1 bis 4 mg II in 26 ml und 0,1 bis 8 mg III in 26 ml Grundelektrolyt besteht Proportionalität zwischen der Wellenhöhe und der Konzentration von II und III. Es können auch II und III neben I polarographisch bestimmt werden, da in Natriumacetat/Methanol und Natriumdiphenyldithiocarbamat die Abscheidungspotentiale der Reaktionsprodukte von II und III wesentlich positivere Werte aufweisen als das des Acetats von I (vgl. Abb. 4). Die vor den Stufen des II und III evtl. auftretenden Wellen werden durch Hydrolyseprodukte von I verursacht und stören keineswegs die Auswertung der Polarogramme. Enthält das Methanol sehr wenig Wasser, so werden diese Stufen nicht beobachtet. Neben 4 mg I lassen sich nach diesem Verfahren noch 4 mg II und 8 mg III je 26 ml Gesamtlösung bestimmen. Bis zu dieser Grenzkonzentration von I–III resultiert auch hier die gleiche zuvorgenannte Proportionalität zwischen Wellenhöhe und Konzentration. In einem Gemisch von I–III wird der Gehalt von I wie üblich komplexometrisch ermittelt. Tetra-n-butylzinn (IV) stört infolge weitgehender Unlöslichkeit in Methanol die Bestimmung von I–III nicht.

Die Möglichkeit einer gleichzeitigen Gehaltsermittlung von IV in I–IV beschränkt sich auf den Chlorsäureaufschluß[15] und anschließende komplexometrische Titration der Zinn(IV)-ionen. IV 1 äßt sich darauf hin nach der Restmethode quantitativ bestimmen.

Anerkennung—Die Untersuchungen wurden auf Anregung des VEB EK Bitterfeld durchgeführt; wir danken dem Betrieb für finanzielle und apparative Unterstützung.

Summary—The determination of di-n-butyltin(IV) dichloride and tri-n-butyltin(IV) chloride in the presence of mono-n-butyltin(IV) trichloride with sodium diphenyldithiocarbamate by d.c. polarography is described. The investigations were made in solutions containing 5% of sodium acetate trihydrate in methanol, which dissolves the dithiocarbamates of the di-n-butyl and tri-n-butyl compounds and shifts the reduction wave of the mono-n-butyl compound to more negative potentials. Within certain limits the wave height is proportional to the concentratlon. In a mixture of the organotin chlorides, mono-n-butyltin trichloride is determined complexometrically. Tetrabutyltin is practically insoluble in methanol and does not interfere in the determinations.

Résumé—On décrit le dosage du dichlorure de di-*n*-butylétain(IV) et du chlorure de tri-*n*-butylétain(IV) en présence de trichlorure de mono-*n*-butylétain(IV) au moyen de diphényldithiocarbamate de sodium par polarographie en courant continu. Les recherches ont été effectuées dans des solutions contenant 5% d'acétate de sodium trihydraté en méthanol, ce qui dissout les dithiocarbamates des composés di-*n*-nutyl et tri-*n*-butyl et déplace la vague de réduction du composé mono-*n*-butyl vers des potentiels plus négatifs. Dans certaines limites, la hauteur de vague est proportionnelle à la concentration. Dans un mélange des chlorures organostanniques, on dose le trichlorure de mono-*n*-butylétain complexométriquement. Le tétrabutylétain est pratiquement unsoluble en méthanol et ne gêne pas dans les dosages.

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COMPLEXOMETRIC TITRATION OF CALCIUM IN THE PRESENCE OF LARGER AMOUNTS OF MAGNESIUM

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Summary—A simple and accurate titrimetric determination of calcium in the presence of larger amounts of magnesium is proposed. Calcium is extracted into a small volume of organic solvent as its glyoxal-bis(2-hydroxyanil) complex, and the calcium is titrated with EGTA. The end-point is sharp, and occurs when the red colour of the organic layer vanishes. This method has been successfully applied to the determination of calcium in sea-water with an error less than 0.1%.

IN the determination of calcium, the presence of a large amount of magnesium gives difficulties. In the field of chemical oceanography, it is necessary to be able to determine accurately and rapidly the calcium content of sea-water, in which the molar concentration of magnesium is five times that of the calcium.

Several complexometric methods have been reported for the determination of calcium in the presence of a large amount of magnesium. In the most common procedure calcium alone is titrated with EDTA at about pH 13 with Murexide[1–3] or Patton–Reeder's reagent (NN)[4] as an indicator. Sometimes, however, this procedure gives large errors owing to co-precipitation of calcium with magnesium hydroxide and adsorption of the indicator on the precipitate. Some attempts have been made to avoid these errors, *e.g.*, drop by drop addition of EDTA solution,[5,6] back-titration,[7] aging of the precipitate,[8] addition of alkali after the addition of EDTA equivalent to 95% of the calcium,[9] and addition of tartrate[10] or sucrose[11] to prevent the precipitation. In the case of sea-water, however, the present authors failed to reduce the error to less than 0·1% by using these proposed methods. Although calcium may be determined with a high accuracy by titrating it after separation from a mixture by ion-exchange chromatography or precipitation as calcium oxalate, the procedure is time-consuming.

When EGTA [ethyleneglycol-bis(2-aminoethylether)-N,N,N',N'-tetra-acetic acid] is used as the titrant[12,13] instead of EDTA, calcium is selectively titrated in the presence of magnesium because of the difference in the stability constants between calcium-EGTA ($\log K_{\text{Ca-EGTA}} = 11{\cdot}0$) and magnesium-EGTA ($\log K_{\text{Mg-EGTA}} = 5{\cdot}2$). Unfortunately, a selective indicator for calcium has not been available for use at pH 10, at which magnesium does not precipitate. This problem has been overcome by several methods. Calcium may be titrated after masking magnesium with tartaric acid,[14,15] or magnesium may be titrated while calcium is masked with EGTA.[16,17] Indirect indicators such as zinc-Zincon,[18,19] zinc-PAN[20] or zinc-Murexide[21] have been used. None of these methods, however, seems to be precise enough to detect subtle variations of calcium concentration in sea-water, because the errors are larger than 0·1%. Culkin and Cox[22] adopted a spectrophotometric titration, using zinc-Zincon indicator.

The present authors have tried to determine calcium directly by a visual titration, with high accuracy, in the presence of larger amounts of magnesium. EGTA is used as a titrant and GHA [glyoxal-bis(2-hydroxyanil)], a sensitive and selective reagent for calcium,[23] is used as metal indicator[24] at pH 11·7. If a suitable organic solvent is added to the solution, the calcium–GHA complex is extracted quantitatively and the interference by the magnesium precipitate formed at this pH is very small.

EXPERIMENTAL

Reagents

EGTA standard solutions. A stock solution, 0·1*M*, was prepared by dissolving 38 g of EGTA in 300 ml of 1*M* sodium hydroxide and diluting with distilled water to 1 litre. Aliquots of this solution were taken to prepare 10*mM* and 5*mM* or more dilute solutions. The EGTA solutions were standardized against pure zinc or magnesium.

Borate buffer. In 500 ml of distilled water were dissolved 10 g of borax, ($Na_2B_4O_7.10\ H_2O$) and 30 g of sodium hydroxide.

GHA solution, 0·05% *in n-propanol.*

n-Butanol or n-amyl alcohol.

Standard calcium solution. Exactly 1·0309 g of pure calcium carbonate dissolved in hydrochloric acid and diluted to 1 litre after the addition of 13·114 g of magnesium sulphate ($MgSO_4.7H_2O$), 0·0243 g of strontium chloride ($SrCl_2.2H_2O$) and 274·67 g of sodium chloride. The solution was 10·30*mM* in calcium, 53·20*mM* in magnesium, 0·091*mM* in strontium and 470*mM* in sodium, as in sea-water.

Procedure

By pipette transfer 20 ml of a sea-water sample into a 100-ml conical beaker and add exactly 20 ml of 10*mM* EGTA. Stirring the solution, add 4 ml of 0·05% GHA and 4 ml of buffer solution. After stirring for 3 min (with a magnetic stirrer) add 7 ml of n-butanol or 5 ml of n-amyl alcohol, extract the red calcium–GHA complex into the organic layer, and titrate with 5*mM* EGTA solution. While adding the titrant, stir the solution vigorously and observe the organic layer occasionally, stopping the stirring near the end-point. At the end-point, the colour of the organic layer changes from red to colourless. The amount of calcium is evaluated by multiplying the titre by an empirically determined correction factor allowing for the magnesium and strontium.

RESULTS AND DISCUSSION

As shown in Table I, the relative standard deviation in the determination of calcium in a sea-water sample was <0·1%. Small amounts of calcium added to a sea-water sample were quantitatively recovered within the limits of analytical error, as shown in Table II.

Effect of other cations

The effects of the major cationic constituents in sea-water were investigated. The results are shown in Table III.

Sodium and potassium. No effects were found in the presence of sodium and potassium at five times the concentrations in sea-water.

Magnesium. The presence of magnesium gave slightly lower values for calcium, *e.g.*, by 0·2% with the same amount of magnesium as in sea-water, and the same decrease was observed with an artificial sea-water containing no strontium. In order to eliminate this small but certain error caused by magnesium, it is necessary either to reduce the concentration of magnesium to less than 0·7 g/l. or to make an empirical correction with the standard calcium solution containing the same amount of magnesium as the sample. The correction factor was +0·23% for the magnesium in sea-water.

TABLE I.—Determination of calcium in sea-water sample*

Sample* *ml*	$9{\cdot}257mM$ EGTA added, *ml*	$4{\cdot}627_6mM$ EGTA in titration, *ml*	Ca + Sr found, *μmole*
20·008	20·002	4·74	$207{\cdot}1_0$
20·008	20·002	4·76	$207{\cdot}1_9$
20·008	20·002	4·74	$207{\cdot}1_0$
20·008	20·002	4·73	$207{\cdot}0_5$
20·008	20·002	4·74	$207{\cdot}1_0$
20·008	20·002	4·76	$207{\cdot}1_9$
Average		4·74	$207{\cdot}1_2$
Standard deviation			0·06

* The water was sampled from the surface of the Pacific at 38°01′N, 143°58′E (salinity = 34·58‰).

TABLE II.—Recovery of calcium added to a sea-water sample*

Sample, *ml*	Ca added, *μmole*	Ca + Sr found,† *μmole*	Recovery of Ca added, *μmole*	%
20·008	0·00	$207{\cdot}1_2$		
20·008	1·99	$209{\cdot}0_9$	$1{\cdot}9_7$	99 ± 7
20·008	3·98	$211{\cdot}0_5$	$3{\cdot}9_3$	99 ± 4
20·008	4·98	$212{\cdot}0_6$	$4{\cdot}9_4$	99 ± 3
20·008	9·95	$217{\cdot}0_0$	$9{\cdot}8_8$	99 ± 2
20·008	19·90	$226{\cdot}8_7$	$19{\cdot}7_5$	99 ± 1
20·008	49·75	$256{\cdot}9_3$	$49{\cdot}8_1$	100·1 ± 0·3

* The sea-water used is the same sample as in Table I.

† Each of the values is the average of five determinations and the 95% confidence limits were ±0·10 μmole.

Behaviour of strontium. As shown in Table IV, a large portion of strontium added to a sample was determined together with calcium and the recovered strontium was always lower than the added amount by about 10%. The recovery depended also on the concentration of magnesium. When the solution contained no magnesium, all of the strontium–GHA complex was extracted into the organic layer and titrated with 100% recovery. When the concentration of magnesium was as high as $0{\cdot}25M$, no strontium–GHA complex was extractable. In the case of sea-water, the effect of strontium can easily be allowed for by comparison with an artificial or standard sea-water of which the chemical composition has been determined, since the concentration of strontium is low and its ratios to calcium and to magnesium are almost constant. The correction factor was −0·77% for the strontium in sea-water. Therefore, the titre for calcium in sea-water must be corrected by multiplying by a factor of 0·9946 (to allow for strontium *and* magnesium). Even taking account of these corrections and other factors reducing the accuracy of the calcium titration, it is unlikely that the error in the determination of calcium in sea-water exceeds 0·1%.

Heavy metals. It is unnecessary in the case of sea-water to consider the effects of heavy metals, because of their low concentration, but the usual masking agents may be used, as shown in Table V.

TABLE III.—Titration of calcium in the presence of major cations in sea-water

Sample, *ml*	[Metal], *mM*	Concentration factor*	[Ca], *mM*	10·187*mM* EGTA used, *ml*	Deviation %
20·00	—	—	10·30	20·23	
20·00	Na, 2350	5	10·30	20·23	0·0
20·00	K, 50	5	10·30	20·22	−0·0
20·00	Mg, 270	5	10·30	19·86	−1·8
20·00	Mg, 108	2	10·30	20·13	−0·5
20·00	Mg, 54	1	10·30	20·19	−0·2
20·00	Mg, 27	0·5	10·30	20·23	0·0
20·00	Artificial sea-water containing no Sr		10·30	20·19	−0·2
20·00	Artificial sea-water containing 0·091*mM* Sr		10·30	20·34	

* The concentration factor for a metal means the ratio of its concentration in the sample to that in sea water.

TABLE IV.—Recovery of strontium added to a sea-water sample*

Sample, *ml*	Sr added, *μmole*	Ca + Sr found, *μmole*	Recovery of Sr added *μmole*	%
20·008	0·0	$207{\cdot}1_2$		
20·008	1·6	$208{\cdot}3_2$	$1{\cdot}2_0$	75 ± 12
20·008	4·0	$210{\cdot}6_7$	$3{\cdot}5_5$	89 ± 4
20·008	8·0	$214{\cdot}2_6$	$7{\cdot}1_4$	89 ± 2
20·008	12·0	$217{\cdot}6_7$	$10{\cdot}5_5$	88 ± 2
20·008	16·0	$221{\cdot}1_2$	$14{\cdot}0_0$	88 ± 1
20·008	20·0	$224{\cdot}8_6$	$17{\cdot}6_4$	88 ± 1

* The sea-water used is the same sample as in Table I.

TABLE V.—Determination of calcium in the presence of heavy metals

Sea-water, *ml*	[Metal] added, *ppm*	Masking agent	Ca + Sr found *mM*
20·00	—	—	$10{\cdot}3_5$
20·00	Co, 100	KCN	$10{\cdot}3_6$
20·00	Cu, 100	KCN	$10{\cdot}3_5$
20·00	Fe(II), 100	KCN	$10{\cdot}3_4$
20·00	Fe(III), 100	KCN	$10{\cdot}3_3$
20·00	Fe(III), 100	TEA*	$10{\cdot}3_2$
20·00	Al, 100	TEA	$10{\cdot}3_3$
20·00	Mn, 50	TEA	$10{\cdot}3_2$

* TEA = triethanolamine.

The metal indicator GHA

GHA is unsuitable in two respects: since the GHA–calcium complex is rather unstable in solution, the titration must be finished as quickly as possible, certainly within 20 min, and the development of the colour being slow, the organic solvent must be added 3 min after the addition of the indicator and the buffer solution. The n-propanol used as the solvent for GHA also facilitates the extraction of the calcium–GHA complex, being miscible with n-butanol or n-amyl alcohol as well as with water. Methanol or ethanol can also be used.

CONCLUSION

If the EGTA solution can be standardized with an error less than 0·05%, the error in the determination of calcium in sea-water by this method is less than 0·1%. Magnesium in concentration below 27*mM* does not interfere, and in greater amounts may be corrected for by calibration with a standard calcium solution containing a known amount of magnesium. Strontium is only partially titrated, but can be corrected for.

The method presented here is not only rapid and accurate but also highly sensitive, because calcium is extracted into a small volume of organic phase, and it is, therefore possible to determine small amounts of calcium in natural waters.

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Résumé—On propose une méthode simple et précise de détermination titrimétrique du calcium en présence de quantités plus grandes de magnésium. On extrait le calcium dans un petit volume de solvant organique sous forme de son complexe avec le glyoxal bis (2-hydroxyanile) et titre le calcium à l'EGTA. Le point final est net, et correspond à la disparition de la coloration rouge de la couche organique. On a appliqué cette méthode avec succès au dosage du calcium dans l'eau de mer avec une erreur inférieure à 0,1%.

Zusammenfassung—Eine einfache und genaue titrimetrische Bestimmung von Calcium in Gegenwart größerer Mengen Magnesium wird vorgeschlagen. Calcium wird in eine kleine Menge organischen Lösungsmittels als Komplex mit Glyoxal-bis(2-hydroxyanil) extrahiert und das Calcium mit EGTA titriert. Der Endpunkt ist scharf und besteht darin, daß die rote Farbe in der organischen Schicht verschwindet. Diese Methode wurde mit Erfolg auf die Bestimmung von Calcium in Meerwasser angewandt; der Fehler war kleiner als 0,1%.

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POLAROGRAPHISCHE BESTIMMUNG DES SCHWEFELS IN BENZIN

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Zusammenfassung—Es wird eine polarographische Bestimmung von Gesamtschwefel, elementarem Schwefel, Schwefelwasserstoff, Thiolen, Thioäthern, Di- und Polysulfiden und Thiophenen in Benzin beschrieben. Die Methode ist auch für die Analyse höhersiedender Fraktionen (bis 250°) geeignet. Außer polarographischen Messungen wurden amperometrische Titrationen und voltammetrische Bestimmungen am hängenden Tropfen durchgeführt. Nach Reduktion zu Schwefelwasserstoff sind bei voltammetrischer Bestimmung $10^{-4}\%$ gerade noch erfaßbar. Für die Bestimmung der einzelnen Verbindungstypen beträgt der kleinste erfaßbare Schwefelgehalt $10^{-3}\%$. Für die Durchführung der Gesamtanalyse wird ein Arbeitsschema vorgeschlagen. Die Genauigkeit liegt bei etwa 5%.

DIE an Vergaserkraftstoffe gestellten hohen Qualitätsansprüche machen eine genaue Analyse der Schwefelverbindungen in Benzinen und Leichtölen erforderlich. In Übereinstimmung mit der Entwicklung neuer Methoden zur Verarbeitung schwefelreicher Rohstoffe wurde die Analytik der schwefelhaltigen Inhaltstoffe durch Methoden bereichert, die neue Maßstäbe für die Genauigkeit und Sicherheit der erhaltenen Ergebnisse setzen.[1] Wir untersuchten, inwieweit es möglich ist, durch polarographische Bestimmungen zuverlässige Ergebnisse bei geringem Zeitaufwand zu erhalten. Wir bestimmten elementaren Schwefel, Schwefelwasserstoff, Mercaptane, Di- und Polysulfide, Thioäther, Thiophene sowie den Gesamtschwefel in Benzin und Leichtöl.

EXPERIMENTELLER TEIL

Geräte

Die polarographischen Messungen wurden mit den Polarographen OH 101 und OH 102 der Firma "Radelkis" Budapest (Ungarn) durchgeführt. Die von uns verwendete Meßzelle (Abb. 1) wurde am hiesigen Institut hergestellt, sie läßt Messungen in einem Lösungsvolumen von 1 bis 15 ml zu. Das Bodenquecksilber wird aus einem Reservoir durch den Ansatz 1 in die Zelle gedrückt. Der Ansatz 2 dient der Inertgasspülung der Lösung. Durch den Dreiwegehahn 3 kann auch der Raum über der Lösung mit Inertgas versorgt werden, so daß stets unter völligem Luftausschluß gearbeitet werden kann. Ein straff sitzender Plexiglasdeckel 4 mit drei oder vier Bohrungen für die Einführung der Tropfelektrode, einer Bezugselektrode, eventuell eines Rührers für amperometrische Titrationen und für die Zugabe weiterer Lösung schließt die Zelle ab. Sämtliche Schlauchverbindungen bestehen aus Polyäthylenschlauch. Zur Beseitigung des gelösten Sauerstoffs wurde Stickstoff (mit weniger als 0,015% Sauerstoff) und Argon (mit weniger als 0,02%Sauerstoff) verwendet.

Die voltammetrischen Bestimmungen wurden in der Meßzelle E 69 der Firma "Radiometer" Kopenhagen durchgeführt. Zur Registrierung dienten die obengenannten Polarographen.

Bestimmung des Gesamtschwefels

Die polarographische Bestimmung des Gesamtschwefels kann einerseits nach Verbrennung der Probe über das entstehende Schwefeldioxid vorgenommen werden, andererseitsüist auch die Hydrierung der Probe und die anschließende

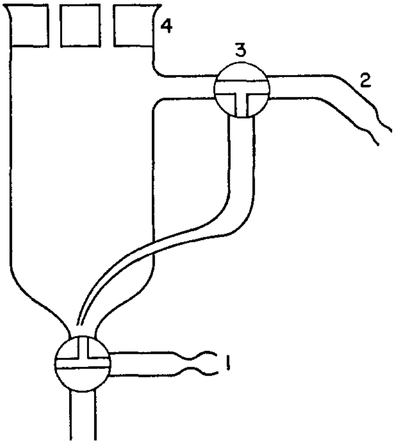


ABB. 1.

Bestimmung des Schwefelwasserstoffs möglich; diese Methode eignet sich besonders für die voltammetrische Bestimmung sehr geringer Schwefelmengen.

Bestimmung des Gesamtschwefels nach Verbrennung zu Schwefeldioxid

Schwefeldioxid wird in saurer Lösung an der Tropfelektrode zu Sulfoxylat reduziert. In Lösungen mit einem $pH < 3,5$ wird eine Reduktionsstufe beobachtet, deren Halbstufenpotential pH-abhängig ist. In 0,1n Salzsäure beträgt es $-0,39$ V (SCE), es verschiebt sich mit steigenden pH um 0,06 V/pH nach negativeren Potentialen. Der Diffusionsstrom ist ebenfalls pH-abhängig und nimmt mit steigender Acidität zu. Im Bereich von 10^{-6} bis 10^{-3} Mol SO_2/l. ist er streng konzentrationsproportional und kann für quantitative Bestimmungen ausgewertet werden. Bei $pH > 3,5$ tritt eine zweite Stufe auf, deren Halbstufenpotential bei $-1,25$ V (SCE) pH-unabhängig ist. Der ersten Stufe entspricht die Reduktion des Schwefeldioxids bzw. des HSO_3^--Ions zu dithioniger Säure, die in SO_2 und H_2SO_2 disproportioniert, letztere wird wahrscheinlich weiter zu elementaren Schwefel reduziert. Diese pH-abhängigen Nachfolgereaktionen bedingen das Ansteigen des Diffusionsstroms mit steigender Acidität. Die Ausbildung der zweiten Stufe entspricht der Reduktion des primär durch Reduktion entstandenen SO_2^--Radikals zu Sulfoxylat.[2]

Durchführung der Bestimmung. Wir verbrannten die Probe nach Gupta[3] in einem Verbrennungsrohr, in dessem Ende sich Kupfergaze befand, um zum Teil gebildetes Schwefeltrioxid zu reduzieren. Die Verbrennungsgase wurden in 5 ml 0,1n Natriumhydroxidlösung aufgefangen, die vorher 10 min mit Stickstoff entlüftet wurden. Diese Lösung wurde mit 1 ml 0,5n Salzsäure neutralisiert und mit Britton-Robinson-Pufferlösung ($pH = 2,0$) auf 10 ml aufgefüllt und zwischen $-0,2$ und $-1,0$ V (SCE) polarographiert. Die Konzentration wird einer Eichkurve entnommen, die durch Verbrennung einiger organischer Schwefelverbindungen bei gleicher Arbeitsweise erhalten wurde. Die Genauigkeit dieser Analyse beträgt $\pm 2\%$.

Bestimmung des Gesamtschwefels nach Hydrierung

Schwefelwasserstoff ergibt in neutraler und saurer Lösung eine anodische Stufe, die der Reaktion des Elektrodenquecksilbers mit Schwefelwasserstoff entspricht. Der Diffusionsstrom ist nur ungenügend reproduzierbar. In alkalischer Lösung läßt sich dagegen Sulfid sehr gut polarographisch bestimmen. Es tritt eine anodische Stufe auf, die auf der Bildung von Quecksilbersulfid beruht. Das Halbstufenpotential ist pH-abhängig und liegt in 0,1n Natriumhydroxid bei $-0,765$ V (SCE). Der Elektrodenprozeß ist völlig reversibel. Die Form der Stufe entspricht einer zweielektronigen-Reaktion. Der Diffusionsstrom ist streng konzentrationsproportional. Die kleinste noch einwandfrei zu bestimmende Sulfidkonzentration ist etwa 10^{-6} Mol/l. Bei höheren Konzentrationen als 10^{-3} Mol/l beobachteten wir eine Aufspaltung der Stufe, wobei die positivere Stufe sich auszubilden beginnt, wenn die negativere einen bestimmten (von den Kapillarkonstanten abhängigen) Wert erreicht. Die Höhe der negativeren Stufe bleibt dann auch bei weiterer Erhöhung der Sulfidkonzentration konstant. Der Gesamtdiffusionsstrom ist auch hierbei der Konzentration proportional. Für die Elektrodenreaktion ergibt sich folgende Gleichung

$$HS^- + OH^- + Hg \rightleftharpoons HgS + H_2O + 2e^-.$$

Das Auftreten der positiveren Stufe bei höherer Depolarisatorkonzentration in Natronlauge erklärt sich unseres Erachtens durch die Bildung eines Sulfidokomplexes an der Tropfelektrode, bei etwas positiveren Potentialen bildet dieser mit der potentialbedingt größeren Quecksilberionenkonzentration an der Elektrodenoberfläche wiederum Quecksilbersulfid. Dieser Stufe entspricht die Reaktionsgleichung

$$\mathrm{Hg} + [\mathrm{HgS_2}]^{2-} \rightleftharpoons 2\mathrm{HgS} + 2e^-.$$

Durchführung der Bestimmung. Die Hydrierung des organisch gebundenen Schwefels kann mit Wasserstoff am Platinkontakt oder nach Granatelli[4] mit Raney-Nickel durchgeführt werden. Tabelle I zeigt einige nach Hydrierung mit Raney-Nickel erhaltene Ergebnisse.

2 g Raney-Legierung werden im Titrierkolben in kleinen Portionen unter kräftigem Rühren in 50 ml 4n Natriumhydroxid gegeben. Nach Beendigung der Wasserstoffentwicklung wird die überstehende Natronlauge abdekantiert und der Katalysator zweimal mit Wasser gewaschen und unter 50 ml Äthanol aufbewahrt. Unter diesen Bedingungen behält der Katalysator seine Aktivität etwa 10 Tage, die Menge reicht für 10 Bestimmungen. Je nach dem zu erwartenden Schwefelgehalt werden 1–6 g Benzin mit Äthanol auf 10 ml aufgefüllt, dann werden 5 ml Katalysatoraufschlämmung zugegeben und das Gemisch in einem 50-ml Kölbchen unter Stickstoffatmosphäre gerührt und auf 60° erwärmt. Nach 15 min werden 10 ml 1n Salzsäure zugegeben und die Lösung beim Sieden gehalten. Der entweichende Schwefelwasserstoff wird in 10 ml 0,1n Natriumhydroxidlösung, die vorher mit Stickstoff gespült wurden, aufgefangen und zwischen $-0{,}5$ und -1 V polarographiert. Die Sulfidkonzentration wird einer Eichkurve entnommen, die mit Natriumsulfidlösungen, besser jedoch mit unter gleichen Bedingungen verarbeiteten Testsubstanzen aufgenommen wurde.

Voltammetrische Sulfidbestimmung

Die hohe Reversibilität des Elektrodenprozesses bei der Reaktion von Quecksilber und Sulfidionen gestattet, diese Reaktion auch voltammetrisch am hängenden Quecksilbertropfen zu verfolgen. Die wie oben vorbereitete Lösung mit einer Höchstkonzentration von 10^{-4} Mol/l $\mathrm{HS^-}$ in 0,1n Natriumhydroxid wurde in die Meßzelle gebracht. Die Anreicherung wurde bei $-0{,}2$ V (SCE) durchgeführt, die Anreicherungszeit zwischen 30 und 600 sec gewählt, die Drehzahl des Rührmotors betrug durchweg 3000 $\mathrm{min^{-1}}$. Die Größe des Quecksilbertropfens wurde auf 4–7 mg eingestellt, das entspricht einer Elektrodenoberfläche von 2 bis 3,2 $\mathrm{mm^2}$. Die Registriergeschwindigkeit lag bei 250 mV/min. Mit der Registrierung wurde konstant 2 min nach Beendigung der Anreicherung begonnen. Der kathodische Strompeak ist der Konzentration und der Anreicherungszeit proportional. Die Reproduzierbarkeit der Ergebnisse ist im Konzentrationsbereich 10^{-4} bis 10^{-7} Mol/l gut, die Genauigkeit beträgt etwa 1,5%. Bei kleineren Konzentrationen wird der Fehler erheblich größer und beträgt im 10^{-8} m-Bereich oft mehr als 20%.

Bestimmung des Schwefels einzelner Verbindungstypen

Im folgenden werden die am häufigsten auftretenden Verbindungstypen des Schwefels in Benzin und Leichtöl auf ihre polarographische Bestimmbarkeit untersucht.

Bestimmung des elementaren Schwefels

Gerber[5] und Hall[6] führten polarographische Bestimmungen von elementarem Schwefel in Erdölfraktionen durch. Gerber arbeitete in schwefelsaurer äthanolischer Lösung und erhielt Stufen mit einem Maximum und einem folgendem Minimum. Der Schwefelgehalt wurde aus dem Diffusionsstrom im Minimum nach einer empirischen Gleichung bestimmt. Hall verwendete als Lösungsmittel Benzol–Methanol–Gemische mit Acetatpuffer als Leitelektrolyt.

Wir untersuchten verschiedene Lösungsmittelgemische und eine ganze Anzahl Leitelektrolyte auf ihre Anwendbarkeit, wobei auf genügende Löslichkeit der Probe, gute Leitfähigkeit, gut ausgebildete Stufen und minimalste Störungen durch andre Schwefelverbindungen Wert gelegt wurde. Am besten haben sich Pufferlösungen mit einem pH von 4,5 bis 6 bewährt. Als geeignetste Lösungsmittel erwiesen sich Äthanol–Isobutanol-, Äthanol–Dioxan- und Methanol–Benzol-Gemische, letztere besonders wegen der Möglichkeit, in derselben Grundlösung auch Thiole und Di- bzw. Polysulfide bestimmen zu können. Das Halbstufenpotential der Reduktionsstufe des elementaren Schwefels liegt in Methanol–Benzol–Wasser (65:30:5), das 0,1n an Acetatpuffer ist, bei –0,62 V (SCE). Mit steigender Acidität verschiebt sich die Stufe zu positiveren Potentialen. Die Elektrodenreaktion ist irreversibel. Der Diffusionsstrom ist in engen Konzentrationsbereichen der Konzentration an freiem Schwefel proportional, über einen größeren Konzentrationsbereich weicht er von der linearen Konzentrationsproportionalität ab (Abb. 2).

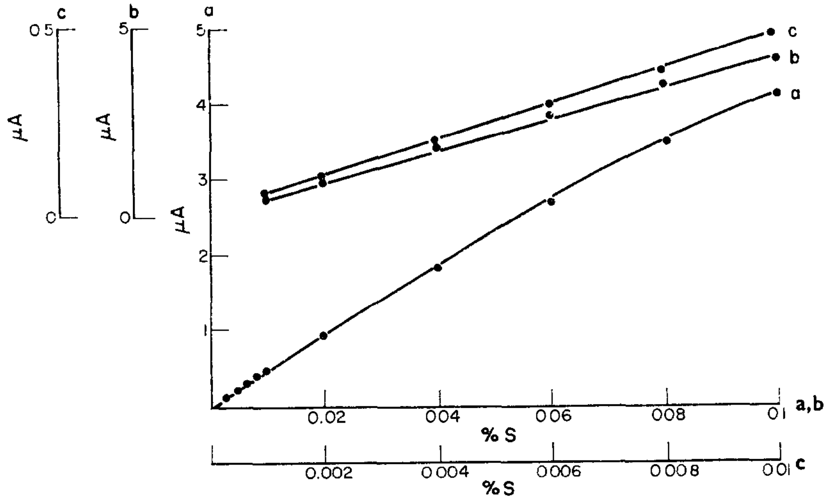


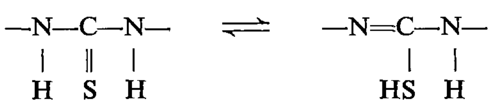
Abb. 2.

In neutralen und alkalischen Lösungen werden unstetige Diffusionsströme erhalten, die in keinem Falle reproduzierbar waren, weil bei der Reduktion infolge zu geringer Wasserstoffionenkonzentration Polysulfidionen entstehen, deren weitere Reaktion sehr langsam verläuft. Die Bildung von Quecksilberpolysulfid an der Tropfenoberfläche erschwert darüberhinaus die Durchtrittsreaktion weiterer Schwefelmoleküle.

Wir stellten eine Lösung staubfeinen monoklinen Schwefels in n-Hexan her, ihre Konzentration war genau 10^{-3} Mol/l. Es wird 0,1–1 ml dieser Lösung mit Elektrolytlösung (0,08n Acetatpuffer in Methanol–Benzol–Wasser; 65:30:5) auf 25 ml aufgefüllt, und 10 ml davon in der Meßzelle 10 Minuten mit Inertgas gespült, das vorher in einer vorgeschalteten Waschflasche mit Lösungsmittel gesättigt wurde. Dann wurde zwischen –0,2 und –1,2 V (SCE) gegen eine gesättigte wässrige Kalomelelektrode polarographiert. Die Eichkurve ist keine Gerade (Abb. 2), die Ergebnisse sind aber gut reproduzierbar. Diese Eichkurve wurde von uns zur Bestimmung des elementaren Schwefels in Benzin und Leichtöl verwendet. Die Stufe des elementaren Schwefels wird nur von aromatischen Disulfiden und Dithiolen gestört, die aber in Benzinen kaum vorhanden sind.

Bestimmung von Schwefelwasserstoff und Thiolen

Nach Gerber[7] ergeben aliphatische Thiole in äthanolischer Lösung (0,025n an Schwefelsäure) zwei anodische Stufen, von denen eine analytisch verwertbar ist. Von Zuman[8] wurden zahlreiche polarographische Bestimmungen der funktionellen Gruppe —NH—CS—NH vorgenommen, deren polarographische Aktivität auf die Tautomerie



$$-\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}-\underset{\mathrm{S}}{\underset{\|}{\mathrm{C}}}-\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}- \quad \rightleftharpoons \quad -\mathrm{N}=\underset{\mathrm{HS}}{\underset{|}{\mathrm{C}}}-\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}-$$

und damit auf die Sulfhydrilgruppe zurückzuführen ist. Wir polarographierten Methan-, Äthan- und n-Butanthiol in wässrigen und alkoholischen Lösungen. Bei Konzentrationen von über 10^{-4} Mol/l. bildeten sich zwei Stufen, deren Gesamthöhe konzentrationsproportional ist. Die im positiveren Bereich liegende Stufe erscheint erst bei Konzentrationen von über 10^{-4} Mol/l., während die negativere Stufe bei dieser Konzentration einen konstanten Grenzwert erreicht. Die Halbstufenpotentiale sind pH-abhängig, das HSP der negativeren Stufe ist auch konzentrationsabhängig. Innerhalb der homologen Reihe der Alkanthiole werden die Halbstufenpotentiale mit größeren Alkylresten nach positiveren Potentialen verschoben. Die Thiole werden dabei nicht oxidiert, es bilden sich Mercaptoverbindungen des Quecksilbers. Bis zu einer bestimmten Konzentration—deren Größe von den Kapillarkonstanten der Tropfelektrode abhängt—werden Verbindungen gebildet, die an der Elektrode adsorbiert werden und die negativere Stufe hervorrufen. Bei höheren Konzentrationen werden Verbindungen gebildet, die von der Elektrode weggeführt werden. Als Grundelektrolyt zur quantitativen Bestimmung der Thiole in Kohlenwasserstoffen kann die gleiche Grundlösung wie zur Bestimmung des elementaren Schwefels verwendet werden. Die Halbstufenpotentiale liegen zwischen —0,4 und —0,5 V(SCE). Die Diffusionsströme der einzelnen Thiole sind bei gleichen Konzentrationen etwa gleichgroß, jedoch wesentlich kleiner als der Diffusionsstrom der Sulfidionen. Da die Sulfidstufe aber im gleichen Potentialbereich liegt, können Thiole neben Schwefelwasserstoff nicht polarographisch bestimmt werden. Selbst für die Bestimmung der Summe von Schwefelwasserstoff und Thiolschwefel kann aus dem Polarogramm höchstens eine größenordnungsmäßige Abschätzung erfolgen. Bei sehr geringen Konzentrationen, bei denen die Thiole nur eine Stufe bilden, ist eine Bestimmung der Summe von Schwefelwasserstoff und Thiolschwefel möglich, weil sich an der Tropfelektrode ein Mercaptoquecksilberion bildet, das entladen und absorbiert wird, so daß der Thiolschwefel die gleiche Menge Quecksilber bindet wie der Sulfidschwefel. Die Elektrodenreaktion verläuft wie folgt

$$RSH + Hg \longrightarrow RSHg^+ + H^+ + 2e^-$$

$$RSHg^+ + e^- \longrightarrow RSHg$$

Wegen der verschiedenen Diffusionsstromkonstanten für Thiole und Schwefelwasserstoff ist es vorteilhafter, die Bestimmung durch amperometrische Titration durchzuführen; dann jedoch nicht in Methanol–Benzol-Lösung, sondern in äthanolischer Lösung.

Es wird 0,1 bis 1 ml der Probe (wir verwendeten eine Lösung von Schwefelwasserstoff und Äthanthiol in n-Heptan) werden in 10 ml äthanolischer Tetraäthylammoniumhydroxidlösung (0,05n), die vorher sauerstofffrei gemacht wurden, gelöst. Bei einem Potential von —1 V (SCE) wurde unter mäßigem Rühren mit 0,005n Quecksilber(II)nitrat-Lösung titriert. Nach Zugabe von jeweils 0,1 ml Titerlösung wurde der Diffusionsstrom aufgezeichnet. Nach Überschreiten des Äquivalenzpunktes steigt der Strom doppelt schnell an, die Genauigkeit beträgt etwa 6%.

Da der Gehalt an Schwefelwasserstoff und Thiolen in Benzinen im allgemeinen sehr gering ist, kann auf diese Weise die Summe beider Schwefeltypen bestimmt werden. Sind die vorliegenden Mengen jedoch größer, so muß eine getrennte Bestimmung erfolgen. Wir führten die Bestimmung ebenfalls amperometrisch durch. Ein aliquoter Teil obiger Lösung wird nach Ansäuren mit einem Tropfen verd. Salzsäure mit äthanolischer Kadmiumnitratlösung (0,005 m) titriert. Dabei wird nur Schwefelwasserstoff erfaßt, die Summe von Thiolen und Schwefelwasserstoff wird im anderen Teil der Lösung durch Titration mit äthanolischer Silbernitratlösung (0,002n) bestimmt.

Bestimmung von Disulfiden

Während in den leichtsiedenden Benzinfraktionen in der Regel keine Disulfide zu erwarten sind, muß mit ihrer Gegenwart trotzdem gerechnet werden, weil sie durch die leichte Oxydierbarkeit der Thiole entstehen können. In Umkehrung dieser Bildung können sie an der Tropfelektrode wieder zu Thiolen reduziert werden. Der Elektrodenprozeß ist eindeutig irreversibel, in Anwesenheit anderer Schwefelverbindungen kann es zu Neben- und Nachfolgereaktionen kommen, die die Reproduzierbarkeit des Diffusionsstroms beeinträchtigen. Die Halbstufenpotentiale einiger Disulfide wurden von Hall[6] und Colichman[9] in einigen Lösungen bestimmt. Mit steigendem pH-Wert der Grundlösung werden die Stufen zu negativeren Potentialen verschoben. Ihre Diffusionsströme sind stark vom Widerstand und von der Wasserkonzentration der Grundlösung abhängig. Mit steigendem Wassergehalt werden die langgezogenen Stufen besser auswertbar, jedoch sinkt dabei die Löslichkeit des Kohlenwasserstoffs stark ab. In alkalischen Lösungen erreicht der Diffusionsstrom seinen Grenzwert erst nach beginnender Reaktion der Grundlösung. Am besten haben sich Pufferlösungen bewährt, die etwa 10% Wasser enthalten und einen pH von 7–9 haben. In der zur Bestimmung des elementaren Schwefels, Schwefelwasserstoffs und der Thiole verwendeten Lösung Methanol–Benzol–Wasser (65:30:5), die als Grundelektrolyt Acetatpuffer ($\mathrm{pH} = 6$) enthält, erhielten wir eine langgezogene flache Stufe, die bei $-0{,}90$ V beginnt und bei etwa $-1{,}4$ V(SCE) ihren Grenzwert erreicht. Die Genauigkeit beträgt etwa 10%. Bessere Ergebnisse erhielten wir in alkoholischer Tetraäthylammoniumperchloratlösung, jedoch kann diese Lösung nur bei Abwesenheit elementaren Schwefels verwendet werden.

Einige Autoren[10,11] halten die amperometrische Bestimmung der durch Reduktion der Disulfide erhaltenen Thiole für die genaueste Bestimmungsmethode für Disulfide, jedoch macht diese Arbeitsweise die Abtrennung aller anderen Schwefel-Verbindungen erforderlich, was sehr aufwendig ist und kaum vollständig gelingen dürfte. Bei Anwesenheit anderer Schwefelverbindungen werden die Ergebnisse völlig unzuverlässig. Da auch die Disulfidkonzentrationen in leichtsiedenden Fraktionen sehr gering sind, ist die direkte polarographische Bestimmung die geeignetste. Als Eichsubstanzen verwendeten wir n-Hexanlösungen von Diäthyl- und Dibutyldisulfid.

Bestimmung der Thioäther

Lukjaniza und Girina[12] erarbeiteten eine Methode zur potentiometrischen Sulfidbestimmung in Erdölprodukten, nach der Prinzler und Toufar[13] gute Ergebnisse bei der Untersuchung sowjetischer Erdöle erhielten. Für Lösungen, deren Sulfidgehalt kleiner als 0,05% ist, konnten wir bei potentiometrischer Endpunktbestimmung keine zuverlässigen Resultate erzielen. Wir versuchten, die gleiche Reaktion amperometrisch zu verfolgen.

Amperometrische Thioätherbestimmung

In der von Lukjaniza zur potentiometrischen Bestimmung der Thioäther mit Jodat vorgeschlagenen Grundlösung (35 ml Benzol, 60 ml Eisessig, 5 ml Salzsäure) erhielten wir bei amperometrischer Titration nur unbefriedigende Ergebnisse. In Analogie zur Reduktion des Nitrations, die bei Gegenwart mehrwertiger Kationen erleichtert wird (Rylich[14]) und demzufolge bei positiveren Potentialen eine Reduktionsstufe gibt, änderten wir die Grundlösung, indem wir den Eisessiganteil durch

Methanol und die als Elektrolyt fungierende Salzsäure durch Calciumchlorid ersetzten. Dieser Lösung wurde vor jeder Bestimmung ein Tropfen methanolischer Cernitratlösung zugesetzt. Dem Verbrauch an Titerlösung entsprechend verläuft die Reaktion nach der summarischen Gleichung

$$2\,RSR + KJO_3 + CaCl_2 + H_2O \rightarrow 2\,RSOR + KCl + JCl + Ca(OH)_2$$

Tabelle II zeigt, daß die erhaltenen Ergebnisse bei Anwesenheit von Thiolen befriedigend sind. Thiophen wird zum Teil mitoxydiert, bei seiner Gegenwart fallen die Sulfidwerte zu hoch aus.

Es wird 1 ml Analysenprobe in 10 ml Grundlösung (30 ml Benzol, 65 ml Methanol, 5 ml 0,5m Calciumchloridlösung) gelöst. Dieser Lösung wird ein Tropfen 0,1m methanolischer Cer(III)-nitrat-Lösung zugegeben. Bei einem Potential von —0,5 V (SCE) wird nach Zugabe von jeweils 0,1 ml 0,01n Kaliumjodat in Methanol-Benzol (2:1) der Diffusionsstrom registriert.

Thioätherbestimmung an der rotierenden Platinelektrode

An der Tropfelektrode zeigen die Thioäther im gesamten zugänglichen Potentialbereich keine Reaktion. Die Oxydation zu Sulfoxiden und Sulfonen erfordert starke Oxydationsmittel. Das Oxydationspotential solcher Reaktionen ist positiver als das Redoxpotential des Quecksilbers, so daß diese Reaktionen an einer Quecksilberelektrode nicht verfolgt werden können. Nicholson[15] oxydierte Thioäther an einer stationären Platinelektrode zu Sulfoxiden. Wir versuchten, eine polarographische Bestimmungsmethode auch für sehr geringe Sulfidmengen an einer rotierenden Platinelektrode zu finden. Wir verwendeten zur Messung die Elektrolysezelle E 69 (Radiometer). Ein in Glasrohr eingeschmolzener Platindraht wurde in den Rührmotor eingeführt, die Stromabnahme erfolgte über einen Schleifkontakt. Als Grundlösung verwendeten wir Methanol–Benzol–Wasser-Gemische mit Salzsäure als Leitelektrolyt. Als Bezugselektode diente ein Silberstab, der unter den gegebenen Bedingungen das reproduzierbare Potential einer Silber–Silberchloridelektrode annimmt.

Die Oxydation beginnt bei 0,85 V. Da bereits bei 0,95 V die Oxydation des Chlorids einsetzt, wird nur bei sehr geringen Sulfidkonzentrationen ein Grenzstrom ausgebildet; meist geht die Sulfidstufe in die des Chlorids über, kann aber von dieser leicht subtrahiert werden, wenn vor der Sulfidbestimmung auch stets die "leere" Lösung polarographiert wird. Die Bestimmung wird durch keine andere Schwefelverbindung gestört. Der Diffusionsstrom ist im Bereich 10^{-6} bis 10^{-3} Mol/l. der Konzentration linear proportional, die Genauigkeit beträgt 2%. Bei der Analyse von Benzin muß jedoch mit einem größeren Fehler gerechnet werden, weil der Diffusionskoeffizient der verschiedenen Thioäther nicht konstant ist. Die Diffusionsströme sind etwa der sechsten Wurzel des Molekulargewichts umgekehrt proportional. Als Eichsubstanz verwendeten wir Thiophan, das in Benzin oft Hauptvertreter der Thioäther ist, dessen Diffusionsstromkonstante mit der des Diäthylsulfides, eines ebenfalls häufig auftretenden Thioäthers, übereinstimmt.

Es wird 10 ml Grundlösung (50 ml Methanol, 50 ml Benzol, 1 ml konzentrierte Salzsäure) von 0,6 V ab nach positiveren Potentialen polarographiert. Dann werden 0,1–1 g der Probe zugegeben und erneut polarographiert. Die Thioätherstufe wird durch Subtraktion des Grundstroms von Diffusionsstrom der Probelösung erhalten. Bei Verwendung von Dimethylsulfoxid als Lösungsmittel und Tetraäthylammoniumperchlorat als Leitsalz werden Stufen mit gut ausgebildetem Grenzstrom erhalten, Perchlorsäure selbst kann ebenfalls als Leitelektrolyt verwendet werden. Die Thioätherkonzentration wird einer Eichkurve entnommen, die mit Thiophan als Eichsubstanz erhalten wurde.

Bestimmung der Thiophene

Jaworski und Bogaczek[16] fanden eine Methode zur polarographischen Thiophenbestimmung in Kohlenwasserstoffen. Thiophen wird mit Wasserstoffperoxid zum Thiophen-1,1-dioxid oxydiert, das überschüssige Wasserstoffperoxid zerstört und das entstandene Dioxid an der Tropfelektrode reduziert. Das Halbstufenpotential liegt bei —1,4 V (SCE). Bei der Oxydation mit Wasserstoffperoxid werden zwar alle anderen Schwefelverbindungen ebenfalls oxydiert, jedoch sind die entsprechenden Oxydationsprodukte (Schwefel, Sulfat, aliphatische Sulfone und Sulfoxide) an der Tropfelektrode nicht reduzierbar, bzw. ist ihr Reduktionspotential (elementarer Schwefel) von dem des Thiophen-1,1-dioxids wesentlich verschieden. Die Methode ist empfindlicher und genauer als die von Stromberg[17] vorgeschlagene amperometrische Titration mit Quecksilbersulfat und verzichtet auf die Abtrennung der Thiophene.

Es werden 0,2 bis 1 g Benzin in 20 ml Dimethylsulfoxid gelöst. Nach Zugabe von 0,2 ml Perhydrol wird die Lösung eine Stunde am Rückfluß im siedenden Wasserbad erhitzt. Nach rascher Abkühlung wird der Lösung 1 ml einer salzsauren 15%igen Titan(III)-chloridlösung zugefügt. Die stark gelbgefärbte Lösung wird mit Tetraäthylammoniumhydroxidlösung bis zur schwach alkalischen Reaktion versetzt, wobei Titanperoxidhydrat ausfällt. Nach Abfiltrieren des Niederschlags wird die Lösung mit 0,1n Tetraäthylammoniumperchloratlösung in Dimethylsulfoxid auf 50 ml aufgefüllt und ein aliquoter Teil nach Belüftung mit Stickstoff zwischen —1,0 und —1,8 V (SCE) polarographiert. Alle Operationen nach Unterbrechung der Oxydation am Rückfluß müssen rasch erfolgen, um das Polarogramm stets nach höchstens 20 min nach Abbruch der Oxydation aufnehmen zu können. Die genaue Einhaltung einer konstanten Zeit zwischen Oxydationsabbruch und Polarographieren ist wegen der Zersetzlichkeit des Thiophen-1,1-dioxids erforderlich. Die Konzentration des Thiophens wird einer Eichkurve entnommen, die mit einer äthanolischen Thiophenlösung unter gleichen Bedingungen aufgestellt wurde.

Gruppenanalyse der Schwefelverbindungen

Während zahlreiche Arbeiten über die Anwendung von Gruppenreagentien berichten, die leider durchweg nicht selektiv sind, orientierten wir uns auf die Arbeiten von Karchmer[10] und Lukjaniza,[1] die auf die Notwendigkeit der stärkeren Beachtung physikalisch-chemischer Methoden hinweisen. Die polarographische Methode ist zur Schwefelbestimmung geeignet, weil sich die meisten Schwefelverbindungstypen einfach und selektiv bestimmen lassen wobei die Kohlenwasserstoffe selbst—auch etwa vorhandene ungesättigte Kohlenwasserstoffe—polarographisch inaktiv sind und somit keine der angeführten Bestimmungen stören. In der folgenden Übersicht ist ein Vorschlag für einen Analysengang gemacht, der sich ausschließlich der polarographischen und amperometrischen Bestimmung der einzelnen Verbindungstypen des Schwefels bedient.

ERLÄUTERUNGEN ZUR POLAROGRAPHISCHEN GRUPPENANALYSE

1. *Gesamtschwefelbestimmung*

1.1 *nach Verbrennung der Probe*

1.1.1 Die Verbrennungsgase werden in 5 ml 0,1n Natriumhydroxid aufgefangen, 1 ml 0,5n Salzsäure und 4 ml Britton-Robinson-Puffer (pH 2 bis 3) zugegeben und polarographiert; oder nach

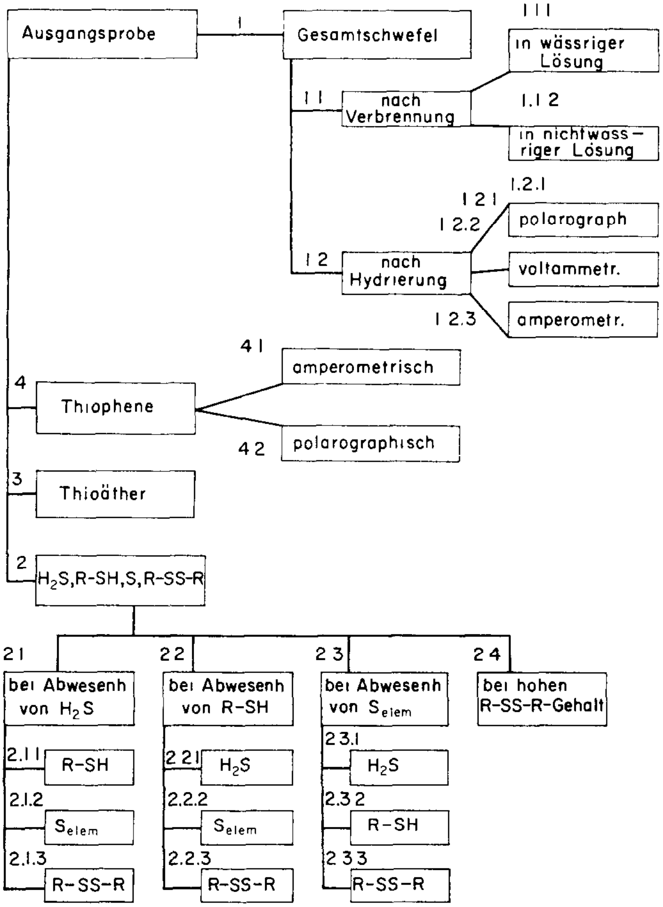
1.1.2 in 10 ml Lösung I aufgefangen und polarographiert. Bei sehr kleinen Schwefelgehalten ist die Bestimmung 1.1.1 in 0,1n Salzsäure wegen der Überhöhung des Grenzstroms empfindlicher.

1.2 *nach Hydrierung*

Die Hydrierung der Probe kann am Platinkontakt oder mit Raney-Nickel erfolgen. In jedem Falle werden die Hydrierungsprodukte in 0,1n Natriumhydroxid aufgefangen und nach

1.2.1 polarographisch oder nach

Schema zur Schwepelgruppenanalyse



1.2.2 voltammetrisch am hängenden Tropfen bestimmt.

1.2.3 Bei der amperometrischen Tritation mit 0,005n Silbernitrat muß die Lösung vor der Titration mit verdünnter Salpetersäure neutralisiert und mit Natriumbicarbonat gepuffert werden.

2. *Bestimmung von elementaren Schwefel, Schwefelwasserstoff, Thiolen und Disulfiden*

Es wird die Probe in Lösung II gelöst und zwischen 0 und —1 V (SCE) polarographiert. Das Polarogramm zeigt folgende Stufen:

—0,4 bis —0,5 V (SCE): H_2S und R-SH

—0,62 V (SCE): $S_{elem.}$ (u. eventuell Polysulfide)

—1,0 bis —1,6 V (SCE): Disulfide

Die Lösung wird auf Anwesenheit von H_2S und R-SH geprüft;

2.1 bei Abwesenheit von H_2S wird das Polarogramm (gegebenenfalls mit größerer Empfindlichkeit) erneut aufgenommen und aus obigen Stufen
  2.1.1 Thiolschwefel,
  2.1.2 elementarer Schwefel und
  2.1.3 Disulfidschwefel
  gegen entsprechende Eichkurven bestimmt. Thiole können auch amperometrisch bestimmt werden:

2.1.1 0,5 ml der Probe werden in 10 ml Lösung III gelöst und mit Lösung IV bei −1,0 V (SCE) titriert.

2.2 Bei Abwesenheit von RSH entspricht die erste Stufe bei −0,4 V der H_2S-Konzentration. Die Bestimmung von H_2S kann entsprechend 2.1 durchgeführt werden. Die Bestimmung von elementaren Schwefel und Disulfiden ist analog 2.1.2 und 2.1.3

2.3 Bei gleichzeitiger Anwesenheit von H_2S und R–SH:

2.3.1 H_2S wird durch Lösung V amperometrisch titriert.

2.3.2 Durch Titration mit Lösung IV wird die Summe von H_2S und R–SH bestimmt, durch Subtraktion der H_2S-Konzentration wird der R–SH-Gehalt ermittelt.

2.3.3 Bei Abwesenheit von elementaren Schwefel wird Disulfid vorteilhaft in Lösung III oder VI polarographiert.

2.4 Bei sehr geringen Konzentrationen von H_2S, R–SH und elementarem Schwefel können größere Disulfidmengen nach Reduktion mit Zink in äthanolischer Lösung als Thiol nach 2.1.1 bestimmt werden; jedoch fallen die Ergebnisse wegen des ständigen Vorhandenseins von Thioäthern, die mit Zink und Eisessig ebenfalls reduziert werden, zu hoch aus.

3. *Thioäther* werden stets in Lösung VII oder I an der rotierenden Platinelektrode bestimmt.

4. *Thiophene* werden bei größeren Schwefelgehalten nach

4.1 in Lösung VIII mit Lösung IX bei −0,5 V (SCE) titriert.

4.2 In Benzinen wird Thiophen in das 1,1-Dioxid überführt, das in Lösung I zwischen −1,0 und 1,8 V (SCE) polarographisch bestimmt wird.

Lösung I: 0,05n Tetraäthylammonium perchloratlösung in Dimethylsulfoxid
Lösung II: 650 ml Methanol, 300 ml Benzol, 50 ml 1n Essigsäure/Natriumacetat
Lösung III: 0,05n Tetraäthylammoniumperchloratlösung in 95%igen Äthanol
Lösung IV: 0,005n Silbernitratlösung in 95%igen Äthanol
Lösung V: 0,005m Cadmiumnitratlösung in 95%igen Äthanol
Lösung VI: 450 ml Methanol, 450 ml Isobutanol, 100 ml 0,5n Lithiumchlorid oder 0,5n Tetraäthylammoniumperchloratlösung
Lösung VII: 500 ml Methanol, 500 ml Benzol, 10 ml konz. Salzsäure
Lösung VIII: 950 ml Äthanol, 50 ml 1n Essigsäure/Natriumacetat
Losung IX: 0,05m Quecksilber(II)-nitratlösung in 95%igen Äthanol

TABELLE I.—GESAMTSCHWEFELBESTIMMUNG

In n-Heptan gelöste S-Verbdg.	% S	Probemenge, *mg*	% S gefunden I	II
Dibenzyldisulfid	0,073	464,7	0,069	0,070
Thiophen	0,081	620,3	0,078	0,079
Thiophan	0,134	504,4	0,128	0,129
Erdölbenzin	0,11	781,0	0,137	0,138

I—Nach einer mit NaSH aufgenommenen Eichkurve.

II—Nach einer Eichkurve, die nach Hydrierung von Dibenzyldisulfid aufgenommen wurde.

TABELLE II.—AMPEROMETRISCHE BESTIMMUNG VON THIOPHAN

Vorgelegte Menge, *mg S/ml*			Amperometrisch bestimmte Konzentration Thiophan,
Thiophan	Thiophen	Äthylthiol	*mg S/ml*
0,0017	—	—	0,002
0,0023	—	—	0,0027
0,0047	—	—	0,0050
0,0071	—	—	0,0074
0,0071	0,028	—	0,0077
0,0142	0,112	—	0,0165
0,0213	0,112	0,032	0,033
0,047	0,063	0,032	0,056
0,047	—	0,064	0,0495
0,047	—	0,256	0,052

Ergebnisse

Wir führten nach diesem Trennungsschema Bestimmungen in einigen Testlösungen und in drei Böhlener Benzinen durch, deren Ergebnisse in den Tabellen III und IV zusammengefaßt sind. Die erhaltenen Ergebnisse sind befriedigend. Eine solche Analyse dauert etwa 8 Stunden.

Table III.—Schwefelgruppenanalyse einiger Testlösungen

Schwefelverbindung	Konzentration, %S					
	Lösung 1		Lösung 2		Lösung 3	
	geg.	gef.	geg.	gef.	geg.	gef.
Gesamt-S	0,363	0,366	0,149	0,144	0,096	0,094
Elem. S	0,013	0,012	0,013	0,012	0,013	0,012
H_2S	0,009	0,008	0,017	0,015	0,009	0,008
R-SH	0,011	0,013	0,044	0,048	0,011	0,013
R-SS-R	0,057	0,052	0,029	0,025	—	0,003
R-S-R	0,103	0,105	0,046	0,046	0,046	0,047
Thiophen	0,170	0,156	—	0,00	0,017	0,014
Gesamt		0,346		0,146		0,098
Abweichung zur Gesamt.-S-Best.		−5,5%		+1,7%		+4,1%

Tabelle IV.—Schwefelgruppenanalyse in einigen Benzinen

Schwefelverbindung	Konzentrationen, %S		
	Erdölbenzin	Reformat	AT-Benzin
Gesamt-S	0,138	0,036	0,059
Elem. S	0,003	0,001	0,002
H_2S	0,002*	0,004*	0,002
R-SH			0,003
R-SS-R	0,012	0,004	0,006
R-S-R	0,073	0,011	0,030
Thiophen	0,055	0,018	0,019
Gesamt	0,145	0,038	0,062
Abweichung zur Gesamt-S-Best.	+5,1%	+5,6%	+5,0%

* Summe von H_2S und R–SH.

DISKUSSION

Die aus Diffusionsstrommessungen erhaltenen Schwefelgehalte sind in Benzinen mit einem größeren Fehler behaftet als in Testlösungen, weil die Diffusionsstromkonstanten der einzelnen Schwefelverbindungen gleichen Typs eine Funktion ihrer Molekulargewichte und deshalb nicht gleich sind. Als Eichsubstanzen müssen die Verbindungen gewählt werden, die in der zu analysierenden Probe als Hauptbestand teil des jeweiligen Verbindungstyps vermutet werden. Die bei der Bestimmung von Disulfiden (und zum Teil auch von elementarem Schwefel) erhaltenen Ergebnisse sind weniger genau, weil sie durch etwa vorhandene Polysulfide, die bei der Reduktion miterfaßt werden, beeinträchtigt sind. Da diese Typen aber nur einen kleinen Teil des Schwefelgehalts ausmachen, fällt diese Ungenauigkeit weniger ins Gewicht.

Summary—The polarographic determination of total sulphur, elemental sulphur, hydrogen sulphide, thiols, di- and polysulphides, thioethers and thiophenes in petrol is described. This method is applicable to the analysis of higher fractions, boiling below 250°. Besides the polarographic measurements, voltammetric determinations and amperometric titrations were carried out. After reduction to hydrogen sulphide, $10^{-4}\%$ total sulphur can be determined directly by voltammetric determination. The minimum determinable concentration of individual species is $10^{-3}\%$. Accuracies of 5% are achieved. An analytical scheme is included.

Résumé—On décrit le dosage polarographique du soufre total, du soufre élémentaire, de l'hydrogène sulfuré, des thiols, des dipolysulfures, des thioéthers et des thiophènes dans l'essence. Cette méthode est applicable à l'analyse de fractions supérieures bouillaent en dessous de 250°. A côté des mesures polarographiques, on a effectué des dosages voltamétriques et des titrages ampérométriques. Après réduction en hydrogène sulfuré, on peut déterminer $10^{-4}\%$ de soufre total par dosage voltamétrique. La concentration minimale dosable d'espèces déterminées est de $10^{-3}\%$. On a obtenu des précisions de 5%. On inclut un schéma analytique.

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POLAROGRAPHIC MICRODETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS AFTER OXYGEN FLASK COMBUSTION

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Summary—A method for the microdetermination of organic compounds containing halogens, by a polarographic finish, is reported. After the combustion of the organic sample in the oxygen flask, the products are absorbed in a suitable absorbent and chemically treated to produce Cl^-, Br^-, BrO_3^- or IO_3^- ions in solution before the polarography. The method is applicable to partially, highly, and fully halogenated aromatic and aliphatic compounds, whether solid or liquid. The results are generally within the acceptable limits of error.

MANY methods are available for the microdetermination of chlorine, bromine, and iodine in partially-halogenated organic compounds,[1-3] but very few for highly or completely halogenated samples.[4] Most of these methods apply, after decomposition by various techniques, a potentiometric[5,6] or a titrimetric finish.[1] The mercurimetric titration of chlorine has been reported[7] to be quite satisfactory. Diphenylcarbazone is used as indicator but the end-point is only clear in 80–90% ethanolic medium. Since Cheng[1] developed this method in 1959, it has become very popular for routine work. Very recently,[4] this method has been applied for the analysis of highly halogenated compounds. For bromine and iodine the iodometric finish either by hypochlorite[2] or Leipert bromine oxidation[8] is preferred over the mercurimetric titration, which is associated with poor conversion factors, particularly for iodine.

The object of the present work was to develop a polarographic finish for the microdetermination of any of the three halogens in compounds whether partially, highly or completely halogenated. Apart from the work of Pražák *et al.*[9] and Novák[10] who used a polarographic finish for the routine semimicro analysis of vinyl chloride copolymers and some other organic substances, no mention has so far been made of a general polarographic method for chloride after oxygen flask combustion. Whereas Pražak *et al.* used electrical combustion, Novák used a primitive oxygen flask closed with a cork stopper. No such work has been carried out for either bromine or iodine.

EXPERIMENTAL

Apparatus

An Orion–KTS 510 Polarograph with accessories was used. The combustion was carried out in an oxygen flask of 500 ml capacity. The electrolytic vessel was an ordinary Kalousek cell with a cathode compartment allowing sample solutions down to 4 ml in volume to be polarographed. The dropping mercury electrode had a drop time of 3–4 sec under an open head of 86 cm of mercury. In the determination of chlorine and bromine as chloride and bromide the anode was filled with mercurous sulphate and 2*M* sulphuric acid; for iodine and bromine estimated as iodate and bromate the anode was a saturated calomel electrode.

The nitrogen used for deaerating the solutions was purified by bubbling the gas through a series of three bubblers containing vanadium(II) chloride solution and amalgamated zinc.

Reagents

All reagents were AR or MAR grade, except where otherwise mentioned, and doubly distilled water was used. Standard solutions (10^{-2} *M*) of MAR sodium chloride, potassium bromide, potassium iodide, potassium bromate and potassium iodate were prepared.

Procedure

The technique of sampling, weighing, and combustion of the organic compounds by the oxygen flask method is similar to that described in Ref. 4. The chloro, bromo, and iodo samples analysed include liquid and solid, aliphatic and aromatic compounds.

For chloride or bromide. Place 7 ml of 0·1*M* sodium nitrite solution in the 500-ml conical flask. Fill the flask with pure oxygen and, just before starting the combustion, add 1·5 ml of 5*M* nitric acid to the flask. After combustion, shake the flask for 5 min and leave it for 2–3 min. Remove the stopper and rinse with twice distilled water. Add one drop of Methyl Red indicator and then 2·5*M* sodium hydroxide until the indicator colour is changed to yellow. Acidify with 0·2*M* sulphuric acid until a red colour just appears, and add two drops more to obtain a pH of 3–4. Transfer the solution quantitatively to a 50-ml standard flask, add 0·2 ml of 0·5% gelatine solution, dilute to the mark and mix. Rinse the clean polarographic cell with a few ml of the solution. Transfer about 5 ml to the cathode compartment of the cell, and pass purified nitrogen gas through it to deaerate the solution. Polarograph the solution with high damping zero compensation of condenser current and a starting potential of +0·10 V and 0·00 V for chloride and bromide respectively, using a 2*M* H_2SO_4–Hg_2SO_4 anode. Use a sensitivity corresponding to 10 and 15 μA full-scale deflection for chloride and bromide respectively.

For bromine as bromate. Place 1·5 ml of 60% sodium hydrochlorite solution and 7 ml of 10% potassium dihydrogen phosphate as absorption solution (pH 6·2) in the 500-ml conical flask. Fill the flask with pure oxygen and ignite the sample as usual. After combustion, shake the flask for 5 min and leave it for 2–3 min. Remove the stopper and rinse with doubly distilled water. Stir the solution for 10 min with a magnetic stirrer. Destroy the excess of hypochlorite by adding 0·2 ml of 80% formic acid. Add one drop of Methyl Red to check for complete removal of hypochlorite. Then add 5*M* sodium hydroxide until a yellow colour is obtained and add 1 ml in excess to give a pH value of about 10. Add 0·2 ml of 0·5% gelatine solution. Transfer the solution quantitatively to a 50-ml measuring flask and dilute to the mark with 0·1*M* sodium sulphate solution; mix. Recording the polarogram of bromate as described under the bromide procedure with a starting potential of −1·3 V *vs*. SCE as anode, and 15 μA full-scale deflection for sensitivity.

For iodine as iodate. Follow the bromate procedure but use 8 ml of 2*N* sodium hydroxide as absorption solution; after combustion, neutralize the solution with 4*N* sulphuric acid (one drop of Methyl Red) until an orange colour appears, then add 1·5 ml of saturated bromine water to oxidize iodide to iodate, destroy the excess of bromine as before and adjust the pH of the solution to 5·2–6 by adding 2·5*M* sodium hydroxide until the orange colour of Methyl Red appears. Use a starting potential of −0·25 V *vs*. SCE as anode.

RESULTS AND DISCUSSION

Chlorine compounds

When sodium hydroxide was used as the absorption solution, correct results (Table I) were obtained only for partially chlorinated compounds with chlorine contents ranging between 17 and 34%. Representative figures are shown in Table I. The average absolute error is ±0·25% and the average recovery is 100·5%. Low recoveries for highly-chlorinated compounds were due to the formation of free chlorine, particularly with sample weights over 4 mg.[4] The use of a reducing absorption solution was necessary. Hydrogen peroxide, which proved satisfactory with the mercurimetric finish,[4] gave rise in the present work to an ill-defined anodic wave, leading to erroneous results, see Fig. 1(a). This is probably due to the difficulty of destroying the last traces of peroxide even on boiling in the presence of a platinum catalyst.

Attention was then directed towards the use of acidic sodium nitrite as absorbent[4] which besides being an efficient reducing agent gave no complications in the polarographic finish, cf. Fig. 1(b) and (c).

The anodic wave of chloride was studied by Revenda[11] and later by Kolthoff and Miller.[12] They stated that there is direct proportionality between the diffusion current and the concentration of the chloride ion up to about $2 \times 10^{-3}M$. Based on an average sample weight of 5 mg of a fully chlorinated compound *e.g.*, hexachloroethane (*ca.* 90% Cl) which has the highest chlorine content of all the compounds analysed (cf. Table II), the expected molarity of the chloride solution used to record the polarogram would be about $2{\cdot}4 \times 10^{-3}M$, which is of the allowable order of magnitude.

TABLE I.—MICRODETERMINATION OF CHLORINE IN PARTIALLY CHLORINATED ORGANIC COMPOUNDS, WITH SODIUM HYDROXIDE AS ABSORBENT

Compound	Weight, *mg*	Cl, % Theory	Cl, % Found	Recovery, %
p-Chlorobenzoic acid	7·00	22·65	22·33	98·6
	6·80		22·92	101·1
p-Chloronitrobenzene	7·33	22·50	22·69	100·8
	7·50		22·72	101·0
p-Chloroaniline	7·80	27·79	28·01	100·8
	6·50		28·11	101·2
2,6-Dichloro-4-nitrophenol	5·67	34·14	34·25	100·3
	4·50		34·50	101·1
1-Chloro-2,4-Dinitrobenzene	6·30	17·50	17·76	101·5
	6·60		17·30	98·8

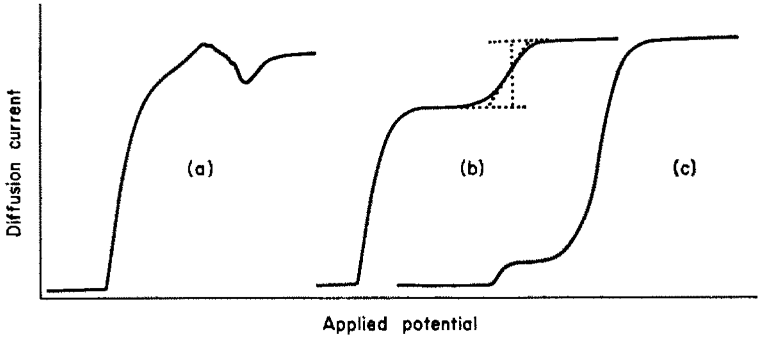

FIG. 1.—Anodic waves of $10^{-3}M$ Cl$^-$.
Absorbent: (a)—NaOH and H_2O_2; (b) and (c)—acidic sodium nitrite.
Sensitivity: (b) 30 μA full-scale deflection; (c) 10 μA full-scale deflection.

In the polarographic finish, the wave-height is equivalent to the volume of titrant in titrimetric analysis, and the sensitivity to the normality of the titrant. Therefore different sensitivities were tried to find the one that produced the best defined wave with maximum height. Figure 1 shows the anodic wave of $10^{-3}M$ chloride recorded at different sensitivities. The half-wave potential, for all the compounds analysed, falls between −0·065 V and 0·075 V *vs.* the 2*M* H_2SO_4–Hg_2SO_4 electrode.

By the acidic sodium nitrite procedure, very satisfactory results (Table II) were obtained for partially, highly, and fully chlorinated compounds. This representative series of aromatic and aliphatic compounds possesses chlorine contents ranging from 17 to 90%. Some of the compounds analysed are liquids, otheis are solid, and some are sublimable and have low melting-points.

The initial test compound *p*-chlorobenzoic acid, available as an organic analytical standard, gave a maximum error of ±0·25% in a series of six determinations.

Nine different compounds analysed by the same procedure gave the results in Table II, with an average absolute error of ±0·24% and an average recovery of 100·1%; the maximum error is ±0·33%.

Table II.—Microdetermination of chlorine in partially, highly, and fully chlorinated organic compounds, with acidic sodium nitrite as absorbent

Compound	Weight, *mg*	Cl, % Theory	Cl, % Found	Recovery, %
p-Chlorobenzoic acid (6 results)	6·32–7·25	22·65	22·39–22·91	100·1
1-Chloro-2,4-Dinotrobenzene	7·85	17·50	17·81	101·8
	7·01		17·70	101·1
m-Chloronitrobenzene	7·82	22·50	22·69	100·8
	7·43		22·39	100·0
p-Chloroaniline	6·62	27·79	28·08	101·0
	5·78		28·02	100·9
p,p-Dichlorobenzophenol	4·57	28·20	27·91	99·0
	4·82		27·96	99·1
p,p-Dichlorodiphenylmethane	4·48	27·96	29·62	98·9
	4·56		29·65	99·0
2,6-Dichloro-4-nitrophenol	5·05	34·14	34·41	100·8
	4·83		34·34	100·6
Chloranil	4·50	57.29	57·82	100·2
	4·60		57·81	100·2
Decachloronaphthalene	2·92	70·27	70·23	99·9
	2·77		70·16	99·8
α,α-Heptachlorotoluene	2·76	74·49	74·56	100·1
	2·66		74·51	100·0
Tetrachloroethylene	3·85	85·51	85·80	100·3
	6·01		85·28	99·7
Hexachloroethane	6·00	89·85	89·95	100·1
	3·45		89·65	99·8

Bromine compounds

Acidic sodium nitrite was also found suitable for determination of bromine as bromide. The anodic wave-height is directly proportional to the bromide ion concentration up to about $5 \times 10^{-3}M$.[11] Among compounds analysed, 5 mg of acetylenetetrabromide (Br 92·5%) would give about $1{\cdot}15 \times 10^{-3}M$ bromide solution for recording of the polarogram. This is well within the working concentration limit of bromide. The half-wave potential ranges between —0·180 and —0·195 V *vs.* the 2*M* H_2SO_4–Hg_2SO_4 electrode.

The standard test compound, *p*-bromobenzoic acid, in 5 analyses (Table III) gave a maximum error of ±0·44%. Eight compounds with bromine content ranging from 40 to 92% gave an average absolute error of ±0·20% and average recovery 100·0, Table III. The compounds included partially, highly, and fully brominated aromatic and aliphatic solids and liquids.

A more successful method for bromine determination was found to be through

TABLE III.—MICRODETERMINATION OF BROMINE IN PARTIALLY, HIGHLY, AND FULLY BROMINATED ORGANIC COMPOUNDS, WITH ACIDIC SODIUM NITRITE AS ABSORBENT, AND REDUCTION TO BROMIDE

Compound	Weight, *mg*	Br, % Theory	Br, % Found	Recovery, %
p-Bromobenzoic acid (5 results)	5·16–7·61	39·75	39·37–40·26	100·2
p-Bromonitrobenzene	6·10	39·56	39·96	101·0
	7·02		39·49	99·8
p-Bromophenol	5·61	46·19	46·51	100·7
	5·45		45·91	99·4
5,7-Dibromo-8-hydroxyquinoline	6·85	52·75	52·88	100·2
	4·87		52·39	99·3
Bromanil	4·10	75·47	75·60	100·2
	6·30		75·39	99·9
Tetrabromo-*o*-xylene	5·70	75·79	75·61	99·8
	5·49		76·10	100·4
Pentabromotoluene	6·63	82·10	82·22	100·1
	4·95		82·20	100·1
Ethylene tetrabromide	4·54	92·49	92·60	100·1
	2·60		92·23	99·7

TABLE IV.—MICRODETERMINATION OF BROMINE IN PARTIALLY, HIGHLY AND FULLY BROMINATED ORGANIC COMPOUNDS AFTER HYPOCHLORITE OXIDATION TO BROMATE

Compound	Weight, *mg*	Br, % Theory	Br, % Found	Recovery, %
p-Bromobenzoic acid	6·30	39·75	39·95	100·5
	5·51		39·32	98·9
	7·46		39·97	100·6
p-Bromonitrobenzene	8·11	39·56	39·45	99·7
	7·70		39·68	100·3
p-Bromophenol	6·20	46·19	46·25	100·1
	5·50		46·26	100·2
5,7-Dibromo-8-hydroxyquinoline	3·25	52·75	52·52	99·6
	7·05		52·79	100·1
Bromanil	3·30	75·47	75·70	100·3
	4·08		75·81	100·5
Tetrabromo-*o*-xylene	6·40	75·79	75·56	99·7
	5·42		76·01	100·3
Pentabromotoluene	5·40	82·10	82·31	100·3
	4·25		82·43	100·4
Ethylene tetrabromide	2·91	92·49	92·13	99·6
	4·90		92·17	99·7

conversion of bromide with hypochlorite oxidation[2] into bromate, which shows favourable amplification on polarographic reduction.

Rylich[13] studied the reduction of the bromate ion at the dropping mercury electrode and found a single wave corresponding to direct reduction to bromide ion:

$$BrO_3^- + 6H^+ + 6e \rightarrow Br^- + 3H_2O.$$

Since the wave-height is proportional to the number of electrons consumed in the reduction process, the wave-height for reduction of bromate is 6 times that for the corresponding amount of bromide. It is worth mentioning that Kolthoff and Orelemann[14] found that the half-wave potential of the bromate wave varies with the pH.

It is therefore advisable to work at a fixed pH range. We used a pH of about 10 at which the half-wave potential falls between −1·8 and −1·85 V *vs*. SCE.

The procedure applied to the analysis of the same series of bromo compounds (Table IV) gave an average absolute error of ±0·22%, average recovery 100·3%, maximum error ±0·43%.

Iodine compounds

Since there is no well-defined anodic wave for iodide, conversion into iodate by the well-known Leipert method[8] is necessary. This allows the use of sodium hydroxide as absorption solution since the combustion products, mainly iodine with some iodate,[7] are ultimately oxidized to iodate.

TABLE V.—MICRODETERMINATION OF IODINE IN PARTIALLY AND HIGHLY IODINATED ORGANIC COMPOUNDS, WITH SODIUM HYDROXIDE AS ABSORBENT AND OXIDATION TO IODATE

Compound	Weight, *mg*	I, % Theory	I, % Found	Recovery, %
o-Iodobenzoic acid (5 results)	3·10–5·48	51·17	50·96–51·52	100·1
8-Hydroxy-7-iodoquinoline-5-sulphonic acid	4·34	36·05	36·01	99·9
	5·41		35·98	99·8
Iodochlorohydroxyquinoline	3·51	41·54	41·68	100·3
	5·78		41·35	99·6
Iodobenzene	2·71	62·20	62·40	100·3
	3·92		62·08	99·8
Iodotoluene	2·95	58·20	58·09	99·8
	3·50		57·97	99·6
Iodoform	2·69	96·69	96·54	99·8
	4·16		96·68	100·0
α,Bromo-β-(3-Iodo-4-methoxyphenyl)-acrylate	1·98	33·13	32·72	98·8
	2·78		33·28	100·4

However, besides the ease of recording the cathodic wave of iodate, the polarographic reduction also presents a six-fold amplification[13] by the mechanism described for bromate. Here also the half-wave potential is sensitive to variation in pH. At the pH range of 5·2–6·0 used in our procedure, the half-wave potential falls between −0·5 and −0·65 V *vs*. SCE.

Five runs on *o*-iodobenzoic acid gave (Table V) a maximum error of ±0·28%. A representative series of 6 compounds with iodine contents ranging from 33 to 97%. (Table V) gave an average absolute error of ±0·15%, average recovery 99·8%, maximum error ±0·38%.

Zusammenfassung—Es wird über eine Methode zur Mikrobestimmung halogenhaltiger organischer Verbindungen mit polarographischem Abschluß berichtet. Nach Verbrennung der organischen Probe im Sauerstoffkolben werden die Produkte in einem geeigneten Absorber aufgefangen und chemisch so behandelt, daß vor der Polarographie in der Lösung Cl^-, Br^-, BrO_3^- oder JO_3^- vorliegen. Die Methode läßt sich auf teilweise, stark und vollständig halogenierte, feste oder flüssige aromatische und aliphatische Verbindungen anwenden. Die Ergebnisse liegen im allgemeinen innerhalb der zulässigen Fehlergrenzen.

Résumé—On rapporte une méthode pour la microdétermination des composés organiques contenant des halogènes, avec fin de dosage polarographique. Après la combustion de l'échantillon organique en fiole d'oxygène, on absorbe les produits dans un absorbant convenable et les traite chimiquement pour produire les ions Cl^-, Br^-, BrO_3^- ou IO_3^- en solution avant la polarographie. La méthode est applicable aux composés aromatiques et aliphatiques partiellement, hautement et complètement halogénés, solides ou liquides. Les résultats sont généralement dans les limites d'erreur acceptables.

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SHORT COMMUNICATIONS

Spot test for the detection of iodate in the presence of periodate Application to the detection of *vic*-dihydroxy compounds

(*Received* 30 *October* 1967. *Accepted* 29 *November* 1967)

THE heteropoly acid 6-molybdic-1-periodic acid has been known for more than 70 years.[1] Although there is little available information about the chemical properties of this compound, it should be possible to mask periodate with molybdate by forming this heteropoly acid. Only one application of this masking reaction is known.[2] Iodate, which does not form a heteropoly acid, can be titrated iodimetrically in the presence of masked periodate because the heteropoly acid does not react with iodide at pH 3. This discovery has several important consequences. Those that are applicable to qualitative analysis are outlined below; some quantitative applications will be published later.

All the tests described below depend on the production of iodine by the reaction of iodide with iodate in the presence of 6-molybdoperiodate in acid solution. The iodine is detected with starch.

Detection of iodate in the presence of periodate

This is the simplest application. By the procedure described below, 0·02 μg of iodate (dilution 1:10^7) can be detected in the presence of at least 0·7 mg of periodate. This is ten times more sensitive than the pyrogallol test for iodate,[3] previously the most sensitive recorded. Chloride, bromide, nitrate, sulphate, fluoride (all 0·1*M*) did not interfere, although occasionally they had a slight effect on the intensity of the colour produced. Iron(II) gave a series of colours, eventually giving a blue solution even in the absence of starch. Copper(II) gave a turbid solution, and lead a yellow precipitate. Calcium had no effect. Obviously there is interference from anions that oxidize iodide, such as bromate and nitrite. This test detected iodate in all analytical-grade samples of potassium and sodium periodate tested, and titration of the iodine with thiosulphate showed that the sodium salt contained 0·2% of iodate.

Application to the Malaprade reaction

The reaction of periodate with *vic*-dihydroxy compounds, especially carbohydrates, to give iodate and sometimes formaldehyde and/or formic acid has been widely applied in qualitative and quantitative analysis. The qualitative applications depend on the detection of formaldehyde[4] or of iodate by precipitation as silver iodate.[5] In the present test the iodate formed is detected by the colorimetric amplification procedure with iodide. A comparison of the sensitivities of the present test applied to tartrates and D-glucose with the sensitivities of other tests is summarized in Table I. In pure solution, 0·1 μg (dilution 1:2 × 10^6) of tartrate could be detected, *i.e.*, the test is 500–1000 times more sensitive than the others. Chloride, bromide, fluoride, nitrate, sulphate (0·1*M*), acetate,

TABLE I.—SENSITIVITY OF TESTS FOR TARTRATE AND GLUCOSE

Method	Tartrate, μg	D-Glucose, μg
IO_4^-; $AgIO_3$ pptn.	50	5
IO_4^-; HCHO detect.	100	25
IO_4^-; IO_3^--I^- react.	0·1*	0·1*
gallic acid-H_2SO_4	2	
thio-Michler's ketone	1	
5-hydroxy-1-tetralone		0·2
triphenyltetrazolium chloride		0·2
Ag_2O reduction		0·1

* Present work; other values from Feigl, *Spot Tests in Organic Analysis*, 7th Ed., pp. 128, 149, 317, 338, 339, 469.

citrate, succinate and oxalate ($2 \times 10^{-2}M$) did not interfere, but in the presence of these anions, the detection limit is 0·3 μg (1:10^6). The detection limit for glucose is 0·1 μg (1:2 × 10^6). Salicylate ($2 \times 10^{-2}M$) interferes; its response is 3% that of an equivalent amount of tartrate.

The spot test can be used in systematic qualitative schemes. Tartrate is precipitated as its calcium salt,[6] along with fluoride and oxalate. The spot test is almost as sensitive when applied to precipitated tartrate as it is with a soluble tartrate, even when oxalate and fluoride (1000-fold excess) are also present in the precipitate.

The *vic*-dihydroxy compounds sucrose, D-mannose, D-lactose, D-arabinose and starch all gave strong positive reactions, whereas ethanol and dilute ($\leqslant 10^{-2}$ *M*) solutions of phenol, resorcinol and benzoate gave no reaction. Larger amounts of phenol, benzoate and resorcinol interfered slightly, and very large (10 mg) amounts of oxalic acid, resorcinol and citric acid, especially when added as solids, caused serious interference. Similar amounts of oxalic acid or sodium dihydrogen phosphate gave a positive reaction with masked periodate–iodide solutions. None of the other compounds mentioned in this paper gave this reaction, except for a much smaller effect with citrate. The interference could be a result of the reaction of molybdate with these compounds, with consequent demasking of the periodate; because of the large amount of molybdate used, a high concentration of demasking agent would be necessary, as was found.

As already indicated, commercial samples of periodate salts contain a small amount of iodate (0·2% in the sample used in this investigation). This is sufficient to give a positive test even in the absence of any dihydroxy compound. This can be allowed for by carrying out a blank test with the periodate solution, and adding dropwise a standard (*e.g.* 10^{-4} *M*) thiosulphate solution until the blue colour is discharged. The same number of drops of thiosulphate is then added to the test solution. Obviously, this procedure limits the sensitivity of the test. The greater the purity of the periodate used, the more dilute can be the thiosulphate used, and the more sensitive the resulting test. The sensitivity of the test for *vic*-dihydroxy compounds would be similar to that for iodate but for the impurity of the periodate.

EXPERIMENTAL

Reagents

Buffered molybdate. A 1*M* solution of analytical-grade sodium molybdate, adjusted to pH 3 with chloroacetate buffer, so that the final solution is 2*M* in total buffer components.

Iodide. 1% aqueous solution of potassium iodide.

Periodate. Freshly prepared saturated aqueous solution of potassium periodate.

Thiosulphate, $10^{-4}M$.

Thyodene indicator. (Hopkin & Williams). Used as the solid.

Other compounds used in the investigation were analytical grade or recrystallized. The common anions were added as their sodium or potassium salts.

Procedures

Test for iodate in the presence of periodate. Mix on a spot-plate one drop each of the test sample, molybdate and iodide solutions. Add Thyodene. A blue colour indicates the presence of iodate.

Test for vic-*dihydroxy compounds.* Blank: mix on a spot-plate one drop each of the periodate, molybdate and iodide solutions. Add Thyodene. If a blue colour develops, add thiosulphate solution dropwise until the colour is discharged. Note the number of drops added. Test: mix on a spot-plate one drop each of the test sample, periodate, molybdate and iodide solutions, followed by the number of drops of thiosulphate used in the blank test. A blue colour indicates the presence of a *vic*-dihydroxy compound.

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Summary—Spot tests for the detection of 0·02 μg of iodate in the presence of 45 mg of periodate, and for the detection of 0·1 μg of *vic*-dihydroxy compounds are described. The tests are based on the iodide–iodate reaction, in the presence of periodate masked by an excess of molybdate.

Zusammenfassung—Tüpfelproben zum Nachweis von 0,02 μg Jodat in Gegenwart von 45 mg Perjodat und zum Nachweis von 0,1 μg *vic*-Dihydroxyverbindungen werden beschrieben. Die Proben beruhen auf der Jodid-Jodat-Reaktion; anwesendes Perjodat wird durch einen Überschuß von Molybdat maskiert.

Résumé—On décrit des essais à la touche pour la détection de 0,02 μg d'iodate en présence de 45 mg de periodate, et pour la détection de 0,1 μg de composés *vic*-dihydroxy. Les essais basés sur la réaction iodure-iodate, en la présence du periodate dissimulé par un excès de molybdate.

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Use of lanthanum and sulphuric acid to suppress interferences in the flame photometric determination of calcium in soil extracts

(*Received* 23 *October* 1967. *Accepted* 22 *November* 1967)

THE use of suppressing agents to control interferences in the flame photometric determination of calcium is now widespread. Dinnin[1] found that strontium and lanthanum were the most satisfactory for this purpose. In this paper the application of lanthanum and sulphuric acid to the estimation of calcium in soil extracts is described.

EXPERIMENTAL

Both 2·5% v/v acetic acid and 1*M* ammonium acetate at pH 7 are employed as soil extractants in this laboratory and were used in the tests. Iron, aluminium and phosphorus were known to interfere with calcium emission although the first two are the more critical in soil analyses. A level of 20 ppm of calcium was adopted for the ammonium acetate tests but 40 ppm was chosen for acetic acid because the latter has the greater extracting power for neutral or base-rich soils. All measurements were made at 422·7 mμ with a Beckman DU spectrophotometer with a flame attachment. Gas pressures of 10 psi oxygen and 3 psi acetylene were adopted. A calibration curve of 0–100 ppm of calcium in 1% v/v sulphuric acid was prepared. Each of the tests described below required recalibration of the instrument with standards containing extractant or lanthanum chloride with or without acid. The calibration curve itself remained valid for all the tests.

RESULTS

The following sequence of tests was carried out.

1. Preliminary investigations showed that each extractant enhanced the emission by approximately 10%.

2. The effects of varying amounts of iron, aluminium and phosphate were tested for each extractant. Table I shows that all three elements depress the emission in both extractants except for phosphate in ammonium acetate. Aluminium interference was the most serious.

3. Initial tests with lanthanum were confined to solutions containing aluminium. A range of 0–2000 ppm of lanthanum (added as the chloride) was tested for 20 or 40 ppm of calcium, 20 or 40 ppm of aluminium and the appropriate extractants. The instrument was recalibrated for each concentration of lanthanum. Table II shows that the lanthanum did not fully suppress aluminium interference under these conditions.

Zusammenfassung—Tüpfelproben zum Nachweis von 0,02 μg Jodat in Gegenwart von 45 mg Perjodat und zum Nachweis von 0,1 μg *vic*-Dihydroxyverbindungen werden beschrieben. Die Proben beruhen auf der Jodid-Jodat-Reaktion; anwesendes Perjodat wird durch einen Überschuß von Molybdat maskiert.

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RESULTS

The following sequence of tests was carried out.

1. Preliminary investigations showed that each extractant enhanced the emission by approximately 10%.

2. The effects of varying amounts of iron, aluminium and phosphate were tested for each extractant. Table I shows that all three elements depress the emission in both extractants except for phosphate in ammonium acetate. Aluminium interference was the most serious.

3. Initial tests with lanthanum were confined to solutions containing aluminium. A range of 0–2000 ppm of lanthanum (added as the chloride) was tested for 20 or 40 ppm of calcium, 20 or 40 ppm of aluminium and the appropriate extractants. The instrument was recalibrated for each concentration of lanthanum. Table II shows that the lanthanum did not fully suppress aluminium interference under these conditions.

TABLE I.—EFFECT OF IRON, ALUMINIUM AND PHOSPHATE ON THE EMISSION OF CALCIUM IN TWO SOIL EXTRACTANTS

	2·5% v/v acetic acid (40 ppm of calcium)			1*M* ammonium acetate (20 ppm of calcium)		
	Apparent calcium, *ppm*			Apparent calcium, *ppm*		
Element added, *ppm*	Iron	Aluminium	Phosphorus	Iron	Aluminium	Phosphorus
0	40	40	40	20	20	20
5	39	37	39	17	19	20
10	37	35	37	17	18	20
20	35	31	34	17	16	21
30	34	27	32	17	15	21
40	34	23	31	16	13	21
50	34	20	31	16	12	21
60	34	18	31	15	11	21

TABLE II.—EFFECT OF LANTHANUM AND SULPHURIC ACID ON THE SUPPRESSION OF THE EMISSION OF CALCIUM BY ALUMINIUM IN TWO SOIL EXTRACTANTS

	2·5% acetic acid 40 ppm of calcium 40 ppm of aluminium		1*M* ammonium acetate 20 ppm of calcium 20 ppm of aluminium	
	Apparent calcium, *ppm*		Apparent calcium, *ppm*	
Lanthanum added, *ppm*	Without 1% H_2SO_4	With 1% H_2SO_4	Without 1% H_2SO_4	With 1% H_2SO_4
400	23	36	17	15
500	25	39	17	18
600	26	39	17	18
700	27	40	18	19
800	27	40	18	20
900	27	42	18	20
1000	27	42	18	20
1500	28	—	18	21
2000	28	44	18	21

4. Test 3 was repeated with the addition of 1% v/v sulphuric acid. Table II shows that lanthanum was fully effective at 800 ppm.

5. Tolerance limits for iron, aluminium and phosphate (expressed as phosphorus) were found in the presence of 800 ppm of lanthanum, 1% v/v sulphuric acid and the extractant. It was found that 50 ppm of aluminium, at least 60 ppm of iron and 50 ppm of phosphorus can be tolerated in acetic acid when 40 ppm of calcium are present. The corresponding figures for ammonium acetate are 20, 30 and 20 ppm when 20 ppm of calcium are present.

6. A recovery experiment was carried out as follows. Duplicate samples of clay, glacial drift, slate and limestone soils were extracted by shaking 10 g of air-dried soil with 250 ml of extractant for 1 hr on an end-over-end shaker. Appropriate aliquots of filtered extract were taken in a 25-ml Pyrex volumetric flask; 10 ppm of calcium, 800 ppm of lanthanum, 1% of sulphuric acid, and the extractant were added before dilution to volume. Solutions without added calcium were similarly prepared. A calibration curve was prepared for 0–40 ppm of calcium in the presence of lanthanum, acid and extractant. The means of the results are presented in Table III and show very satisfactory recovery of 10 ppm of calcium.

7. Finally the flame procedure with and without lanthanum was compared with an EDTA titration method very similar to that of Mackereth[3] except that the end-points were estimated photometrically. The mean results are presented in Table IV and indicate a favourable agreement between the two methods.

TABLE III.—THE RECOVERY OF 10 ppm OF CALCIUM ADDED TO THE EXTRACTS OF FOUR SOIL TYPES (800 ppm OF LANTHANUM AND 1% v/v SULPHURIC ACID PRESENT)

Soil type	2·5% v/v acetic acid			1*M* ammonium acetate		
	Total calcium, *ppm*	Original calcium, *ppm*	Calcium recovered, *ppm*	Total calcium, *ppm*	Original calcium, *ppm*	Calcium recovered, *ppm*
Clay	31·0	21·0	10·0	34·6	24·6	10·0
*Limestone	28·5	18·5	10·0	23·8	13·8	10·0
Glacial drift	13·4	3·6	9·8	13·7	3·8	9·9
Slate	12·3	2·0	10·3	11·5	1·6	9·9

* Extracts diluted 10-fold before addition of calcium

TABLE IV.—COMPARISON OF FLAME PHOTOMETRIC AND EDTA PROCEDURES

	2·5% v/v acetic acid		1*M* ammonium acetate	
	Calcium (*mg/100* g of air-dried soil)		Calcium (*mg/100* g of air-dried soil)	
Soil type	Flame	EDTA	Flame	EDTA
Clay	66	68	77	83
Limestone	430	443	328	339
Glacial drift	11·3	10·5	11·9	12·3
Slate	6·3	6·9	5·0	6·0

These results show that when soil extracts are analysed for calcium, 800 ppm of lanthanum are required to suppress interferences likely to be encountered in most natural soils. This treatment is effective only in the presence of dilute sulphuric acid. The procedure given in test 6 can therefore be recommended when calcium is excited in an oxy-acetylene flame. The efficiency of the sulphuric acid was not investigated for cooler flames with this instrument because these are less sensitive for estimating calcium.

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Summary—Interference by iron, aluminium and phosphate in the flame photometric determination of calcium in soil extracts is not fully suppressed by lanthanum unless dilute sulphuric acid is also present. The investigation was restricted to the oxy-acetylene flame.

Zusammenfassung—Die Störungen der flammenphotometrischen Bestimmung von Calcium durch Eisen, Aluminium und Phosphat werden durch Lanthan nur dann ganz unterdrückt, wenn auch Schwefelsäure anwesend ist. Die Untersuchung beschränkte sich auf die Sauerstoff-Acetylen-Flamme.

Résumé—Les interférences du fer, de l'aluminium et du phosphate dans la détermination du calcium par photométre de flamme dans les extraits de sol ne sont pas totalement supprimées par le lanthane, à moins qu'il n'y ait également présence d'acide sulfurique dilué. Les recherches ont été limitées à la flamme oxy-acétylénique.

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The solubility of ^{14}C-labelled barium carbonate in aqueous systems

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EXPERIMENTAL

Materials

^{14}C-LABELLED barium carbonate was purchased from the Volk Radiochemical Company and had a specific activity of 2.1 curies/mole. Emission spectroscopic examination of this material showed the presence of only negligible quantities of other alkaline earth elements. The material was prepared from 98% pure ^{14}C-labelled carbon dioxide and reagent grade barium hydroxide. The probability of any significant concentrations of soluble barium salts being present is therefore very slight.

Reagent grade barium chloride was obtained from the Fisher Scientific Company.

Strongly alkaline solutions were prepared by diluting filtered 50% sodium hydroxide solution. Measurement of the carbon dioxide liberated on acidification of this 50% solution showed that its carbonate concentration was 0.0047*M*. In the solutions diluted for use, the carbonate concentration was $4.7 \times 10^{-7}M$.

All solutions were prepared in boiled distilled water and handled under nitrogen.

The pH of solutions was determined with Beckman one-drop (calomel–glass) or combination probe (silver–silver chloride–glass) type electrodes.

Apparatus and technique

Approximately 5 mg of ^{14}C-labelled barium carbonate were placed in about 30 ml of solution which already contained the other components. This mixture was shaken in a 200-ml two-necked flask for up to 55 hr. At least 23 hr were needed to assure equilibrium in all cases studied.[1] Nitrogen was continuously passed over the mixture and in most experiments a Beckman probe (silver–silver chloride–glass) electrode was inserted to facilitate continuous pH measurements. The samples were filtered through Millipore absorbent pads until constant activity was noted; usually one or two filtrations were needed, but solutions containing no added hydroxyl ions sometimes required four or five filtrations. A filter pad was never used for more than one filtration. The fact that constant activities were obtained after successive filtrations is indicative of no interaction between solute and filter pad. After filtration, 1 ml of sample and 1 ml of scintillator (POPOP, PPO) were dissolved in about 15 ml of dioxan and counted in a Nuclear Chicago Liquid Scintillation Counter. Counter efficiencies varied between about 30 and 40% and were determined by the 2-channel quench method.

RESULTS AND DISCUSSION

The results are shown in Table I. In solutions to which no base was added, the equilibrium pH was about 9. This is lower than that calculated from the solubility product K_{sp}, for barium carbonate

TABLE I.—SOLUBILITY OF LABELLED BARIUM CARBONATE AND CALCULATED K_{sp} VALUES

Sample	Agitation time hr	pH	Activity *dpm/ml*	μ	$[HCO_3^-]$, *M*	$[CO_3^{2-}]$, *M*	$[Ba^{2+}]$, *M*	$\gamma_\pm^2$	K_{sp}
1*	45	11.35	139431	0.0022	2.2×10^{-6}	2.7×10^{-5}	2.9×10^{-5}	0.67	5.2×10^{-10}
2*	42	11.65	139260	0.0045	1.1×10^{-6}	2.8×10^{-5}	2.9×10^{-5}	0.58	4.7×10^{-10}
3*	45	11.72	157610	0.0052	1.1×10^{-6}	3.2×10^{-5}	3.3×10^{-5}	0.55	5.8×10^{-10}
4†	40	11.35	3194	0.0054	4.9×10^{-8}	6.2×10^{-7}	1.0×10^{-3}	0.55	3.4×10^{-10}
5†	46	11.35	2992	0.0054	4.6×10^{-8}	5.8×10^{-7}	1.0×10^{-3}	0.55	3.2×10^{-10}
6†	39	11.30	1700	0.0120	2.9×10^{-8}	3.3×10^{-7}	3.3×10^{-3}	0.44	4.8×10^{-10}
7†	30	11·30	944	0.0120	1.6×10^{-8}	1.8×10^{-7}	3.3×10^{-3}	0.44	2.6×10^{-10}
8	41	8.8	568595	0.0003	1.2×10^{-4}	4.1×10^{-6}	1.2×10^{-4}	0.92	4.5×10^{-10}
9	36	9.0	292250	0.0002	5.8×10^{-5}	$3{\cdot}3 \times 10^{-6}$	6.2×10^{-5}	0.94	1.9×10^{-10}
10	23	9.3	373535	0.0002	7.1×10^{-5}	7.9×10^{-6}	7.9×10^{-5}	0.94	5.9×10^{-10}
11‡	34	8.7	626233	0.0048	1.3×10^{-4}	3.6×10^{-6}	1.3×10^{-4}	0.56	2.6×10^{-10}
12‡	55	8.9	551418	0.0048	1.1×10^{-4}	5.0×10^{-6}	1.2×10^{-4}	0.56	3.4×10^{-10}

* Base added to system initially.

† Ba^{2+} (as $BaCl_2$) and base added to system initially.

‡ Ionic strength increased with 0.0048*M* potassium chloride.

(5.5×10^{-10}) cited by Butler[1-3] or that determined in highly basic solutions in this work. This increase in acidity was attributed to the reaction of the slightly basic solution with the Pyrex flask. Every possible precaution was taken to exclude carbon dioxide. It is probable that peptization of solid barium carbonate was minimal even in these solutions, since the pH was approximately 9 in both cases and the ionic strength was relatively high in one case. This is supported by the fact that the average result for these solutions was lower than that of the rest.

In these calculations the ratio[2]

$$\frac{[HCO_3^-]}{[CO_3^{2-}]} = \frac{1.783 \times 10^{-4}}{[OH^-]}$$

was used and isotope effects were neglected. In all systems except those in which barium was added as barium chloride $[Ba^{2+}]$ was set equal to the concentration of ^{14}C in the solution since a barium ion could only pass into solution if accompanied by a ^{14}C-atom in the form of a carbonate or bicarbonate ion. Activity coefficients were taken from Butler.[3]

Exchange studies

An additional set of samples was prepared by placing about 1 mg of ^{14}C-labelled barium carbonate in solutions that were 0.001, 0.1, and $1M$ in sodium carbonate. Complete exchange was expected and it was hoped to determine the specific activity of the barium carbonate in this way, but the activities corresponded to an exchange less than 10% and did not increase with time . It was deduced that the crystal surfaces of the barium carbonate became disproportionately populated with unlabelled CO_3^{2-} ions and the equilibrium then involved essentially only these unlabelled ions.

In the studies involving added barium ions, the pH was also increased by adding the appropriate volume of filtered 50% sodium hydroxide solution. The carbonate in these solutions, before dissolution of barium carbonate, was therefore $4.7 \times 10^{-7}M$. Inclusion of this additional carbonate concentration in the calculations for these results, however, gave a K_{sp} value 2 or 3 times greater than that obtained for the other systems. When this additional carbonate concentration was not used in the calculations, a K_{sp} consistent with those for the other systems was obtained. It is probable, therefore, that this additional carbonate was precipitated by the excess of barium present and the resultant drop in specific activity was negligible.

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Summary—The solubility of ^{14}C-labelled barium carbonate has been determined in basic aqueous solutions with and without added Ba^{2+} present and in aqueous solutions containing no added Ba^{2+} or OH^- ions. By use of activity coefficients from the literature, K_{sp} has been determined to be $4.0 \times 10^{-10} \pm 0.5 \times 10^{-10}$ at 25°.

Résumé—On a déterminé la solubilité du carbonate de baryum marqué ^{14}C en solutions aqueuses basiques avec et sans addition de Ba^{2+} et en solutions aqueuses sans addition d'ions Ba^{2+} ou OH^-. En utilisant les coefficients d'activité de la littérature, on a établi que le K_{sp} est de $4{,}0 \times 10^{-10} \pm 0{,}5 \times 10^{-10}$ à 25°.

Zusammenfassung—Die Löslichkeit von ^{14}C-markiertem $BaCO_3$ wurde in basischen wäßrigen Lösungen mit und ohne Zusatz von Ba^{2+} sowie in wäßrigen Lösungen ohne zugesetzte Ba^{2+}- und OH^--Ionen ermittelt. Mit Hilfe von Aktivitätskoeffizienten aus der Literatur wurde K_{sp} zu $4 \cdot 10^{-10} \pm 0{,}5 \cdot 10^{-10}$ bei 25° bestimmt.

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Determination of sodium in high purity silica by activation analysis*

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In the past few years, the use of high-purity materials has grown rapidly. One such use is the incorporation of high-purity silica "windows" in re-entry vehicles. Since silica is transparent to high-frequency electromagnetic radiation, the window is used for transmission and reception of high-frequency signals such as radar. Thus, during acceleration, flight, or re-entry, signals are transmitted to and from a space vehicle to provide for execution of present commands, for data acquisition, for manoeuvering and other uses.

The presence in silica of low ionization potential elements such as sodium, potassium, strontium and some rare earths is undesirable, even in trace quantities. During re-entry, the thermal energy available is sufficient to cause ionization of these elements, which in turn produces an ion sheath about the window. The amounts of these elements present in the silica had to be determined in order that signal distortion or interference as a function of impurity level might be defined. Since sodium was by far the most prevalent of the low ionization potential elements, it was chosen as the representative impurity for the quantitative determinations, *i.e.*, the relatively large quantities of sodium would have the greatest effect on the ion sheath during re-entry.

In a silica matrix, the determination of sodium by standard techniques is, at best, tedious, time-consuming and sometimes inaccurate.[1] There exists a distinct danger that dissolution of the sample and subsequent analysis will introduce a higher sodium impurity than the sample originally contained. However, instrumental neutron-activation analysis does not include any chemical operations and minimizes sample handling; it therefore provides a simple, relatively fast means for determining sodium in silica. The general technique of activation analysis for sodium is described elsewhere.[1]

EXPERIMENTAL

Apparatus

Polyethylene rabbits
TMC 400-Channel analyser
Sodium iodide crystal (Tl activated) 3 × 3 in.
The Sandia Engineering Reactor Facility (SERF) (thermal flux of approx 2×10^{10} neutrons/cm^2/sec in the irradiation position used in this work).

Procedure

The window material was received in block form and a representative sample was obtained by taking slices of the material. Surface sodium and organic contaminants were removed by rinsing with dilute nitric acid and triply distilled water, firing the sample at 400° and rinsing again with nitric acid and triply distilled water; the sample was then dried in an oven at 110°, and crushed to about 50-mesh. As predicted by the work of Kenna and Van Domelen,[2] 1-g samples, placed in polyethylene rabbits, did not exhibit self-shielding effects. The rabbits were made of high-purity polyethylene and exhibited no detectable activity after 24-hr irradiation. The encapsulated NBS standards (Table I) and samples were irradiated for 2 hr in the Sandia Reactor Facility with a thermal neutron flux of 2×10^{10} neutrons/cm^2/sec, removed and allowed to "cool" for periods ranging from 1 to 30 hr. Figure 1 presents a typical γ-ray spectrum obtained at various times after irradiation. Either the

TABLE I.—DETERMINATION OF SODIUM IN NBS STANDARDS

NBS Standard	Na, *ppm* × 10^{-3}	
	Certificate	Experimental
80	123·6	123 ± 2
91	62·9	63·2 ± 1·1
102	0·557	0·545 ± 0·010
Sodium oxalate	344	352 ± 6

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1·37 or 2·75 MeV gamma photopeaks of the ^{24}Na can be used for the analysis. In the present work, the 2·75-MeV photopeak was analysed with a 3 × 3 in. NaI(Tl) crystal and associated electronics attached to a Technical Measurements Corporation 400 channel analyser. Because of the relatively high purity of the silica, no significant amounts of extraneous activity interfered with the ^{24}Na determinations. However, with other types of samples which could produce interfering activities, spectrum stripping techniques could be used. Empty polyethylene rabbits were irradiated simultaneously with the samples and were used as blanks to make background counting corrections. The total nett counts in the 2·75-MeV sample photopeak were compared with the total nett counts in the 2·75-MeV standard photopeak to obtain the sodium content of the sample.

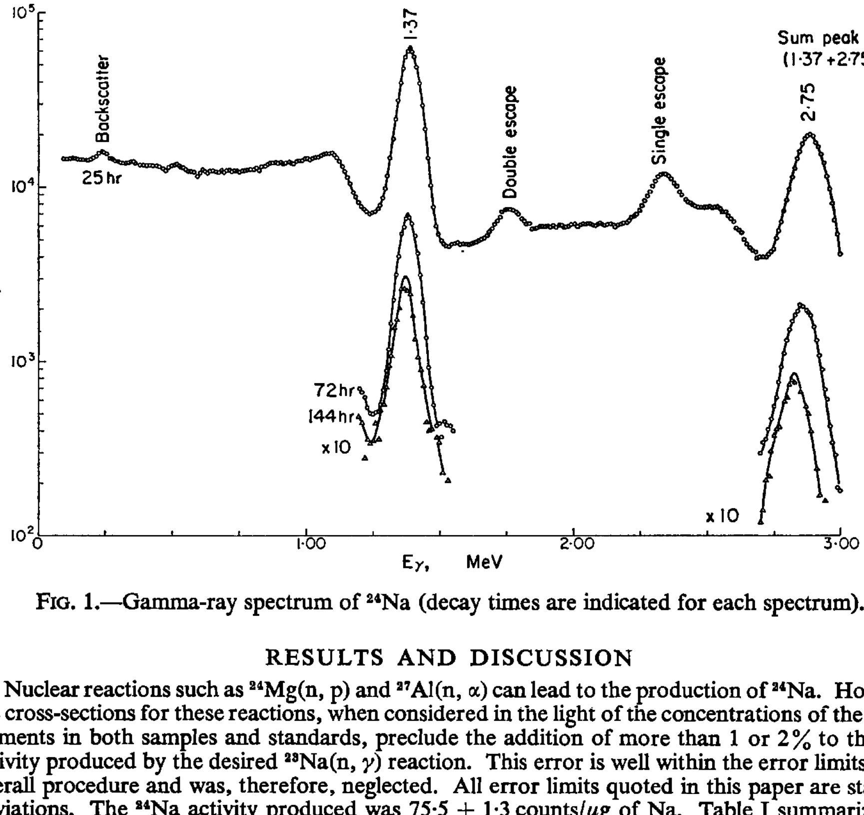

FIG. 1.—Gamma-ray spectrum of ^{24}Na (decay times are indicated for each spectrum).

RESULTS AND DISCUSSION

Nuclear reactions such as ^{24}Mg(n, p) and ^{27}Al(n, α) can lead to the production of ^{24}Na. However, the cross-sections for these reactions, when considered in the light of the concentrations of the parent elements in both samples and standards, preclude the addition of more than 1 or 2% to the ^{24}Na activity produced by the desired ^{23}Na(n, γ) reaction. This error is well within the error limits of the overall procedure and was, therefore, neglected. All error limits quoted in this paper are standard deviations. The ^{24}Na activity produced was 75·5 ± 1·3 counts/μg of Na. Table I summarizes the results from determining sodium in NBS silica standards. Sample weights varied from 0·5 to 500 mg, and the experimental values are averages of three or more determinations. These results show that instrumental neutron-activation analysis is valid and sufficiently accurate for determining sodium in silica.

Other methods have been used to analyse a silica window sample for comparison purposes. The results for sodium were: flame photometry, 43 ± 1 ppm; emission spectroscopy, 56 ± 5 ppm; neutron-activation analysis (Analyst 1), 50 ± 1 ppm; neutron-activation analysis (Analyst 2), 58 ± 3 ppm. The agreement is quite good, particularly when one considers that four independent laboratories used three different methods to obtain the results.

Both pre- and post-flight silica window materials are now routinely analysed by the method described. The sodium contents vary from 3 ± 0·2 to 200 ± 7 ppm. If 24-hr irradiations are used, the sensitivity is calculated to be about 0·5 μg of sodium.[3]

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Summary—High purity fused silica samples and NBS standards were irradiated in the Sandia Reactor Facility for 2 hr at a thermal flux of 10^{10} neutrons/cm²/sec. ^{24}Na was produced by the reaction ^{23}Na(n, γ)^{24}Na (14·9 hr half-life, $\sigma = 0{\cdot}5$ barn), and decayed with emission of 1·37 and 2·75 MeV γ-rays. With the stated flux and irradiation time, sodium at the 3 ppm level has been determined with a standard deviation of 0·2 ppm. Values obtained by thermal neutron-activation analysis agree well with results obtained by emission spectrography and flame spectrophotometric methods.

Zusammenfassung—Proben von hochreinem geschmolzenem Quärz und Standards vom NBS wurden im Sandia-Reaktor 2 Stunden bei einem thermischen Fluß von 10^{10} Neutronen/cm²/sec bestrahlt. ^{24}Na wurde durch die Reaktion ^{23}Na(n, γ)^{24}Na (Halbwertszeit 14,9 h, $\sigma = 0{,}5$ barn) erzeugt und zerfiel unter Emission von Gammastrahlung mit 1,37 und 2,75 MeV. Mit dem angegebenen Fluß und obiger Bestrahlungszeit wurde Na im Bereich um 3 ppm mit einer Standardabweichung von 0,2 ppm bestimmt. Die mit thermischer Neutronenaktivierung erzielten Werte stimmen gut überein mit den Ergebnissen emissionsspektrographischer und flammenspektrophotometrischer Methoden.

Résumé—On a irradié des échantillons de silice fondue de haute pureté et des étalons NBS dans le Sandia Reactor Facilitypendant 2 h avec un flux thermique de 10^{10} neutron/cm²/sec. ^{24}Na a été produit par la réaction ^{23}Na(n, γ)^{24}Na (demi-vie 14,9 h, $\sigma = 0{,}5$ barn) et désintégré avec émission de rayons gamma de 1,37 et 2,75 MeV. Avec les flux et temps d'irradiation annoncés, on a dosé le sodium à la teneur de 3 p.p.m. avec un écart type de 0,2 p.p.m. Les valeurs obtenues par analyse par activation de neutrons thermiques sont en bon accord avec les résultats obtenus par les méthodes de spectrographie d'émission et de spectrophotométrie de flamme.

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DETERMINATION OF TRACE AMOUNTS OF SCANDIUM BY ATOMIC ABSORPTION SPECTROSCOPY

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Summary—Optimum instrumental conditions were investigated for the determination of trace quantities of scandium by atomic-absorption spectroscopy. Enhancement effects by organic solvents and by complex extractions were also studied. ^{46}Sc was used to establish the optimum extraction conditions. A sensitivity of 0.06 ppm of Sc was observed when using extraction into oxine–butanol and atomic absorption was measured with an acetylene–nitrous oxide flame.

BECAUSE of high sensitivity, minimum sample preparation and relative freedom from interference, atomic-absorption spectroscopy has become an ideal technique for the analysis of trace elements. Since the introduction of nitrous oxide as the supporting gas, many elements that form refractory oxides in the presence of oxygen or air can now be determined. Scandium can thus be determined by using nitrous oxide and acetylene mixtures to provide a non-oxidizing flame of high temperature. The population of ground-state scandium atoms essential for absorption depends on several instrumental operation parameters which include ratios of gas mixtures, current intensity of the cathode spectral source, slit-width of the monochromator, and sample solution medium.

The present paper describes studies of optimum operational conditions and enhancement of sensitivity by the use of organic solvents and extraction of complexes.

EXPERIMENTAL

Apparatus

A Techtron A.A. 4 atomic-absorption spectrophotometer was used with a high temperature burner (Techtron AB-40) of 5 cm flame-length. Acetylene was used as fuel and nitrous oxide as supporting gas. The spectral source was a scandium hollow cathode lamp manufactured by Atomic Spectro Lamps of Australia. During operation, the instrument was set at 5× scale expansion to give maximum sensitivity. The 3911·8 Å line of scandium was chosen for absorption measurements.

Reagents

Standard scandium solution. "Spec-pure" scandium oxide (Koch-Light, England) was dissolved in warmed concentrated hydrochloric acid. The solution was evaporated to dryness on a water-bath and the scandium chloride residue was taken up in distilled water. Working standards containing 1–5 μg of scandium per ml were prepared by subsequent dilution of the stock solution.

Procedure

Investigation of optimum instrumental conditions. A 4-ppm aqueous solution of scandium was used to investigate the optimum conditions.

Solvent extraction of scandium. The ^{46}Sc isotope was used to investigate the complex formation and the optimum solution conditions for extraction into various organic solvents. Aliquots (10 ml) of aqueous solution containing *ca.* 0·1 μC of ^{46}Sc (with 2 μg of scandium carrier) were adjusted to various pH values with hydrochloric acid or ammonia and were extracted by 10 ml portions of organic solvents containing the complexing agent, by shaking for 1 min in a separating funnel. The organic phase was separated and a suitable aliquot was taken for scintillation counting of the gamma activity against a standard to calculate the extraction efficiency.

The extractions by various solvents were then carried out under the optimum conditions indicated by the radiometric results. A 5-ml aliquot of solution containing 5 μg of scandium was adjusted to the optimum pH and 5 ml of the extracting agent were added. After the extraction, the organic phase was separated and sprayed into the flame for absorption measurement.

RESULTS AND DISCUSSION

Effect of acetylene and nitrous oxide ratio

Variation in the flame mixture resulted in great variation of the absorption responses. It can be seen from Fig. 1 that the flame temperature was critical in the production of free atoms of scandium. When the nitrous oxide pressure was increased, the flame temperature was also increased. More scandium atoms were excited and the absorption signal was lowered. On the other hand when the flame was too rich in acetylene, the temperature was not sufficient to dissociate the compounds and the absorption signal also decreased considerably. The optimum condition for maximum absorption was at 20 psi pressure of nitrous oxide and a reading of 9·5 on the acetylene flow-meter. With this ratio of gases, the flame was slightly fuel-rich, the "red feather" above the burner slit being about 5 cm long. Such flame conditions effectively increased the proportion of scandium atoms in the ground state.

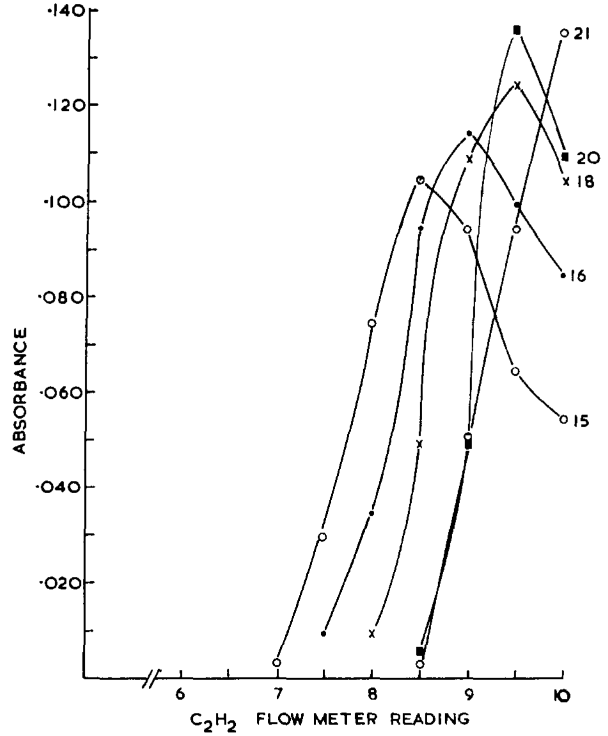

FIG. 1.—Effect of acetylene–nitrous oxide ratios on atomic absorption response. Solution sprayed, 4 μg Sc/ml; lamp current 10 mA; slit-width 50 μ. Figures accompanying curves indicate nitrous oxide pressure in psi.

Optimum instrumental conditions

A hollow-cathode lamp current of 10–12 mA gave maximum response.

The slit-width was chosen to give maximum absorption signal and to compromise between sensitivity and reproducibility of readings. For an operating current of 10 mA, a slit-width of 50–75 μ was considered optimum.

Effect of solvents

Several workers[1–4] have reported the enhancement of sensitivity caused by spraying the sample element in an organic solvent into the flame, or by addition of organic solvents to the aqueous sample solution. For solvents miscible with water, such as the light alcohols, dioxan and acetone, the increase in sensitivity caused by their addition was almost counterbalanced by the dilution of the sample. For solvents immiscible with water, the enhancement was more effective because the element was extracted into the organic phase and a concentration effect was introduced.

The enhancement of absorption sensitivity by addition of hydrochloric acid, EDTA and various water-miscible solvents to a scandium solution was studied by adding 3 ml of solvent to 20 μg of scandium in a 5-ml volumetric flask. The volume was made up to the mark with water, and the solution was sprayed into the flame. The results indicated that all alcohols enhanced absorption and the degree of enhancement depended on the amounts of alcohols added. Hydrochloric acid decreased absorption, the effect increased with increasing amounts of acid used. EDTA was also observed to enhance the absorption signal, 3 ml of 0·1M EDTA (disodium salt) being added. The enhancement of atomic absorption was probably due to the formation of the scandium-EDTA complex which decomposed much more easily in the flame than the ionic scandium species.

Although better sensitivity was obtained in alcohols, for practical purpose, EDTA would seem more desirable. The aqueous solution of EDTA is a better solvent and takes up most inorganic scandium compounds.

The addition of 1 ml of 0·1M EDTA was sufficient for 20 μg of scandium in a final volume of 5 ml.

Solvent extraction of scandium complexes

Investigations were carried out with the ^{46}Sc isotope to establish the optimum solution conditions for complexation and extraction of scandium into various solvents. The optimum conditions were then used for extraction of scandium for absorption measurements. The optimum condition for each complex extraction and the corresponding atomic-absorption response are shown in Table I. Maximum sensitivity was obtained by extraction with butyl alcohol containing 2·5% of oxine at pH 1–4. The sensitivity was found to be 0·06 ppm for 1% absorption.

Extraction procedure

To 5 ml of aqueous solution containing the scandium, add dropwise 1M acetic acid until the pH is 2–3, and shake the mixture in a separating funnel for 1 min with 5 ml of butyl alcohol containing 2·5% of oxine. Centrifuge the solution and withdraw the organic phase for spraying into the flame. Measure the absorption

TABLE I.—MAXIMUM EXTRACTION OF SCANDIUM IN VARIOUS SYSTEMS

System	pH	Extraction, %	Absorbance
2·5% oxine IBMK*	2–4	93	0·060
2·5% oxine in amyl alcohol	2–5	98	0·186
2·5% oxine in butyl alcohol	1–4	98	0·285
2%† APDC/IBMK	4–5	23	0·080
Satd. dibromo-oxine in IBMK	4–5	2	0·200
Aqueous standard, Sc 4 μg/ml			0·140

* IBMK-isobutyl methyl ketone.

† APDC-ammonium pyrrolidinedithiocarbamate.

with reference to a blank of butyl alcohol containing 2·5% oxine. The blank is generally very low.

Interferences in the extraction method

No interference was observed in the absorption response of a 4 ppm scandium solution containing 100 ppm of each of the following elements: U, Fe, Ni, Co, Cu, Mn, Zn, Mo, Pb, Cr, Na, Ca, Mg. Anionic interference, which occasionally happens, can also be eliminated by the extraction procedure.

Zusammenfassung—Die optimalen instrumentellen Bedingungen zur Bestimmung von Scandiumspuren durch atomare Absorptionsspektrometrie wurden ermittelt. Auch Verstärkungseffekte durch organische Lösungsmittel und durch Extraktion von Komplexen wurden untersucht. Zur Ermittlung der besten Extraktionsbedingungen wurde ^{46}Sc verwendet. Bei Extraktion in Oxin-Butanol und Messung der Atomabsorption in einer Acetylen-Lachgas-Flamme wurde eine Empfindlichkeit von 0,06 ppm Sc beobachtet.

Résumé—On a étudié les conditions instrumentales optimales pour le dosage du scandium à l'état de traces par spectroscopie d'absorption atomique. On a aussi étudié les effets d'exaltation par des solvants organiques et par complexe d'extraction. On a utilisé ^{46}Sc pour établir les conditions optimales d'extraction. On a observé une sensibilité de 0,06 ppm en utilisant l'extraction en oxine-butanol et l'absorption atomique a été mesurée avec une flame acétylène-protoxyde d'azote.

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SEPARATION AND IDENTIFICATION OF SOME NATURALLY OCCURRING ALKYLPHENANTHRENES

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Summary—Different separation methods, especially gas chromatography, were applied to crude retene obtained from pine-wood tar. The relative retention times on three different columns, and the melting points, were used to identify the following compounds besides retene itself: 1-methylphenanthrene, 2-ethylphenanthrene, 1,7-dimethylphenanthrene, 1-methyl-7-ethylphenanthrene, 9,10-dihydroretene and possibly 1,3-dimethyl-7-ethylphenanthrene, 1,3-dimethyl-7-isopropylphenanthrene. All the substances formed aerosols at the outlet of the gas chromatograph. Superfine glass wool was found to be an excellent means of coagulating these aerosols.

PINE-WOOD tar contains about 20% retene, 1-methyl-7-isopropylphenanthrene ($C_{18}H_{18}$), which is obtained from the tar as brownish yellow cakes of crude retene. It was found interesting to examine this crude retene by means of gas chromatography and to try to identify and purify some of the compounds present besides the retene.

In 1963 Solo and Pelletier[1] published a list of the relative retention times for a number of alkylphenanthrenes. They used in the main three different stationary phases for the columns, namely SE–30, a methylated silicone rubber, QF–1, a fluorinated silicone oil, NPGS, neopentylglycolsuccinate, and in addition in a few cases Apiezon L, Dow 11 and Dow 710. For the present work SE–30, QF–1 and NPGS were chosen because they were most widely used by Solo and Pelletier. It was necessary to use a further method of identification, since the retention times of the compounds alone did not provide a satisfactory basis for identification, especially as the retention times for certain alkylphenanthrenes differ very little.

Attempts were therefore made to separate the components of the crude retene by means of a series of recrystallizations from ethanol. The separation was carried out in six steps, following a scheme for triangular separation,[2] and gave seven fractions. A small amount of 98% pure retene was obtained, whilst the other compounds did not separate well. Other methods of separation were tried, such as zone-melting.[3] For this purpose an apparatus was used, the oven of which had four speeds, *viz.*, 6·6, 11·4, 20·0 and 40·0 mm/hr. The distance traversed by the oven was about 200 mm and the temperature was kept at 115–120°. Twenty zone passes were carried out on crude retene at a speed of 11·4 mm/hr. Samples were taken at different points along the zone-refining tube and analysed individually in a gas chromatograph, but no difference could be found in the composition of the various samples. The incomplete separation may be explained by the fact that these alkylphenanthrenes have very similar crystal lattices; moreover they form solid solutions as a result of which the possibilities for separation by means of zone-melting are reduced.

The method finally used was a combination of recrystallization from ethanol and preparative gas chromatography. The preparative gas chromatographic separation had to be carried out at different stages because a single separation did not give a satisfactory result. The disadvantage of this method is that only small amounts of the pure material are obtainable and therefore the separation has to be combined with a means of identification requiring small sample weights only. The most convenient means was found to be melting point determination with a Kofler hot-stage microscope.[4] This requires sample weights of only 10 μg. Melting points were determined for the alkylphenanthrenes and for their picrates.

EXPERIMENTAL

Apparatus

Gas chromatographs. Perkin–Elmer 800 and F/6, both with flame-ionization detectors; Aerograph Autoprep and 200, both with thermal conductivity detectors.

Column materials

SE–30 methyl silicone rubber from General Electric, Inc., U.S.A.
D.C. QF–1 (F.S. 1265) fluorinated silicone from Applied Science Lab., Inc., U.S.A.
NPGS, neopentylglycolsuccinate, Applied Science Lab., Inc., U.S.A.
Gaschrom Z 100–120 HMDS treated, Applied Science Lab., Inc., U.S.A.
Embacel 60–100 acid-washed kieselguhr, May and Baker Ltd., England.
Glass wool, Billesholm Antinoise, superfine glass wool with 1·0–1·5 × 10^{-3} mm fibre diameter.

Chemicals

Authentic samples. 1-Methyl-7-ethylphenanthrene and 2-ethylphenanthrene kindly supplied by Dr. F. Piozzi, Politecnico di Milano.

1,7-Dimethylphenanthrene kindly supplied by Dr. O. E. Edwards, Division of Pure Chemistry, National Research Council, Ottawa, Canada.

Phenanthrene, 1-methylphenanthrene, dihydroretene and retene from our own laboratory.

Columns for the gas chromatographs

1. Stainless steel column, $\frac{3}{8}$in. × 20 ft, stationary phase 30% SE–30 on 60–80 mesh Chromosorb. Manufactured by Wilkens Instrument and Research, Inc., and used in the Aerograph Autoprep.
2. Stainless steel column, $\frac{1}{4}$in. × 6 ft, stationary phase 20% SF–96 on 60–80 mesh firebrick. Manufactured by Wilkens Instrument and Research, Inc., and used in the Aerograph 200.
3. Copper column, $\frac{1}{8}$in. × 2 m, stationary phase 10% QF–1 on 100–120 mesh Gaschrom Z; used in the Perkin–Elmer 800.
4. Copper column, $\frac{1}{8}$in. × 2 m, stationary phase 10% NPGS on 100–120 mesh Gaschrom Z; used in the Perkin–Elmer 800.
5. Copper column, $\frac{3}{16}$-in. × 2 m, stationary phase 3% SE–30 on 100–120 mesh Gaschrom Z; used in the Perkin–Elmer F/6.
6. Copper column, $\frac{1}{8}$in. × 5 m, stationary phase 5% SE–30 on Embacel 60–100 mesh; used in the Perkin–Elmer F/6.
7. Copper column, $\frac{3}{16}$-in. × 2 m, stationary phase 20% lithium chloride on Embacel 60–100 mesh, prepared according to Favre and Kallenbach;[5] used in the Perkin–Elmer F/6.

Procedure

Separation. Crude retene gave the chromatogram shown in Fig. 1, with 6 peaks *A–F*, when analysed with column 5 in the P.E. F/6 gas chromatograph, the carrier gas flow-rate being 30 ml of nitrogen/min. The column temperature was 190° and the injection temperature 250°.

The separation of crude retene into its components had to be performed in four stages. The following description of the separation is illustrated by Fig. 2.

Separation stage I. The amount of the main component of the crude retene was reduced by means of three successive recrystallizations from ethanol. The initial amount was 8 g of raw retene dissolved in 100 ml of hot ethanol (99·5%). On cooling to room temperature, 4 g precipitated and were filtered off; the filtrate was evaporated to half the original volume, cooled, and filtered. The third such crystallization gave about 1 g of material enriched with the impurities of the crude retene. The gas chromatogram in Fig. 2 stage I, shows the composition of this material.

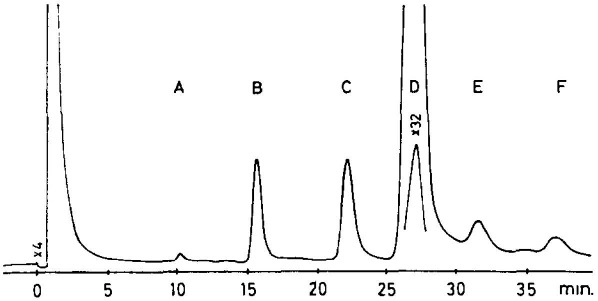

FIG. 1.—Gas chromatogram of crude retene (P.E. F/6, column 5, column temperature 190°C).

Separation stage II. The separation of the material from stage I was carried out in the Aerograph Autoprep, and is shown by the vertical dotted lines in the gas chromatogram in Fig. 2 stage I. The 1 g of material from stage I was dissolved in 5 ml of acetone, and 100 μl of this solution were injected manually with a 100 μl Hamilton syringe into column 1. The column temperature was programmed to rise from 225° to 250° at 0·5°/min. The temperature of the detector and injection block was maintained at 285°. The carrier gas was helium at a flow-rate of 100 ml/min. One separation cycle took 50–60 min. The fractions were collected manually in the standard bottles belonging to the apparatus. To prevent the fractions from partly condensing, a collector-elbow heater was mounted on the tube between the detector and the bottle to maintain the temperature in the outlet tube at about 225°.

The fractions formed aerosols in the collecting bottles and showed an obvious tendency to pass through without coagulating. All fractions showed a similar tendency. Attempts were made to coagulate the aerosols through freezing, but these were not successful. The most effective means of achieving coagulation was a plug of superfine glass wool in the bottle. This caused the aerosols to coagulate completely even at room temperature. Afterwards it was easy to extract the material from the glass wool with acetone.

The gas chromatograms in stage II of Fig. 2 show the results obtained from the analyses of the fractions IIa–IIf.

Separation stage III. Each of the fractions IIa–IIf was separated in the same way as the material from stage I, giving the fractions IIIa–IIIf. The analyses of these are shown in the gas chromatograms in stage III of Fig. 2.

Separation stage IV. The fractions IIIa–IIIf were separated in the Aerograph 200. Column 2 was used. The flow-rate of carrier gas was 60 ml of hydrogen/min. The column temperature was programmed to rise from 230° to 250° at 0·5°/min. The injection block and detector were both maintained at 275° and the filament current was 150 mA. Samples (1 mg dissolved in 15 μl of acetone) were injected with a 50-μl Hamilton syringe. The fractions IVa–IVf were collected in glass capillaries, 100 mm long and 1·3–1·7 mm bore, connected to the detector outlet by a silicone rubber gasket. The capillaries were changed manually between fractions.

When the gaseous compounds from the detector outlet passed the temperature gradient in the capillary at the gasket, they formed aerosols which passed through the capillary without coagulating. When a short plug of superfine glass wool was placed in the capillary in the temperature gradient at the gasket, the aerosols coagulated without staying in the glass wool, but crystallized in the cooler part of the capillary free from the glass wool. The advantage of this arrangement over placing the glass wool in the cooler part of the capillary was that it was possible to remove the glass wool from the capillary without touching the crystals, and the need to extract the crystals from the glass wool before determination of the melting point could thus be avoided.

The amount obtained in each capillary was 0·1–0·3 mg, which was used for the determination of the melting point of the compound and the synthesis of the picrate. The chromatograms in stage IV of Fig. 2 give the results obtained from the analyses of the fractions IVa–IVf, carried out on the material already used for the determination of the melting points. The material on the microscope slides was dissolved in acetone and drawn up with a 10 μl Hamilton syringe. With this method the amounts of sample injected varied slightly from one fraction to another.

Identification

Two methods of identification were used; comparison of the retention times and determination of the melting points. In addition it was possible with some of the peaks to make a direct comparison with an authentic sample in the gas chromatograph.

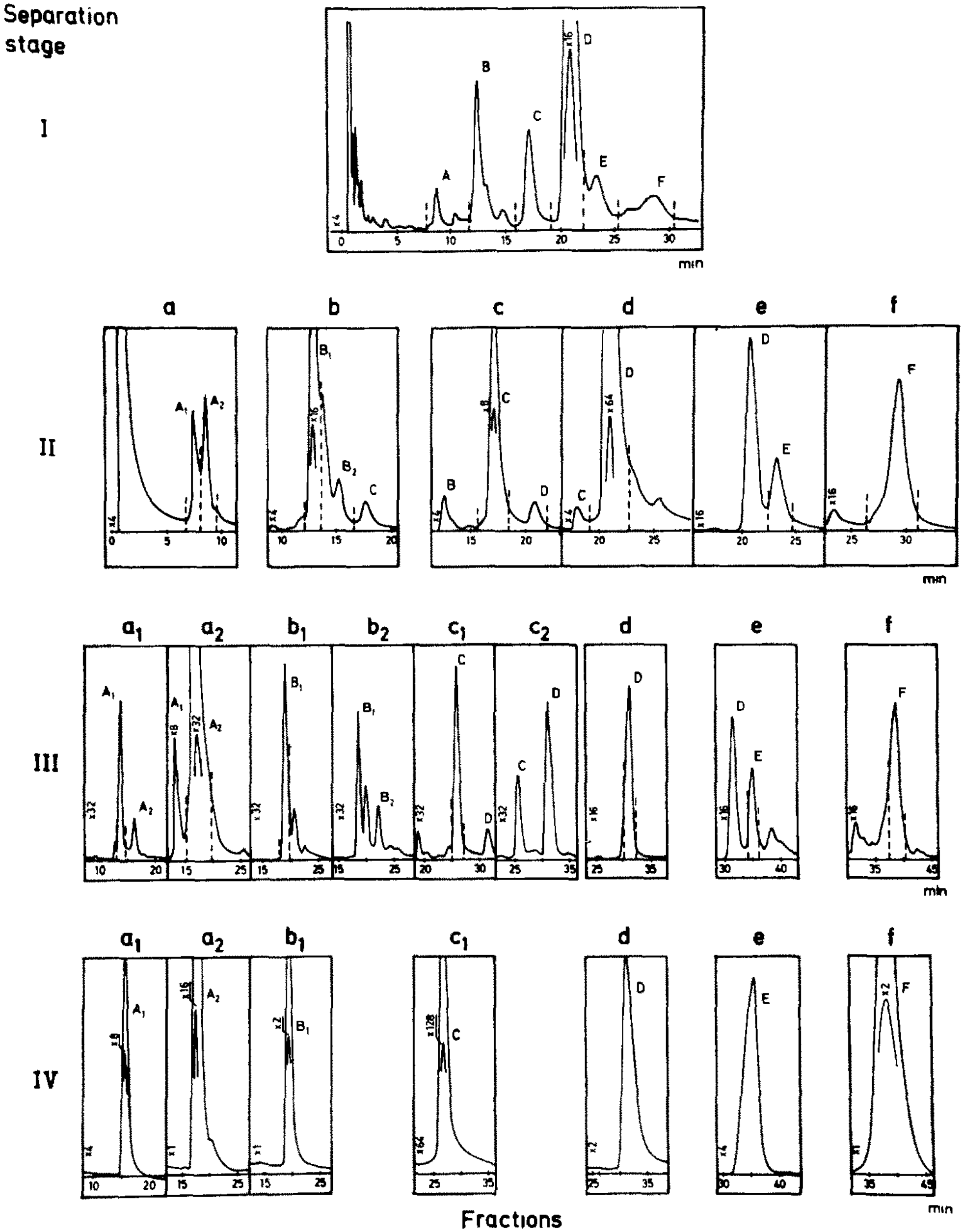

FIG. 2.—Separation scheme for crude retene into compounds A_1–F. The gas chromatograms show the analyses of the different fractions.

Analyses run on P.E. F/6 with 0·1% solutions in acetone. Column temperature 200°C, injection temperature 275°C, nitrogen carrier-gas at 30 ml/min in column 5 for stages I and II, and 15 ml/min in column 6 for stages III and IV.

Relative retention times. Since the temperatures of elution used in this work differ from those used by Solo and Pelletier,[1] the comparison of our data for peaks *A* to *F* with their definitive list of relative retentions demands adjustment of our values. Solo and Pelletier have shown that for each of the solvents used, the data for retention relative to phenanthrene for elution at two temperatures are related by

$$\log (r_S)_{T_1} = \alpha \log (r_S)_{T_2}$$

i.e.,

$$(r_S)_{T_1} = (r_S)^{\alpha}{}_{T_2}$$

Hence to carry out the conversion, two internal standards are needed to eliminate α; phenanthrene and retene were chosen. We may now write

$$r_S = r_t{}^{\alpha} \quad \text{and} \quad R_S = R_t{}^{\alpha}$$

where r_t = the measured retention for some substance relative to phenanthrene
r_S = r_t recalculated to the temperature used by Solo and Pelletier
R_t = the measured retention of retene relative to phenanthrene
R_S = R_t as measured by Solo and Pelletier.

Then

$$\log r_S = \alpha \log r_t$$

$$\log R_S = \alpha \log R_t$$

and

$$\log r_S = \frac{\log r_t \,.\, \log R_S}{\log R_t}$$

The fractions IIIa to IIIf were used for the determination of the retention times of the peaks *A–F*, because each peak was the main component in its fraction at this stage. The determinations were carried out on three different column phases, SE–30, QF–1 and NPGS, chosen in accordance with Solo and Pelletier's list. Column 3 was used in the P.E. 800 with a carrier gas flow-rate of 25 ml of nitrogen/min, and a column temperature of 190° for peaks *A–D* and 220° for peaks *E* and *F*. Column 4 was used in the P.E. 800; carrier gas flow-rate 25 ml of nitrogen/min; column temperature 200° for peaks *A–D* and 210° for peaks *E* and *F*. Column 6 was used in the P.E. F/6; flow-rate of the carrier gas 15 ml of nitrogen/min; column temperature 200° for all peaks. The injection temperature was 250° for all three columns, and 1-μl samples of 1% acetone solutions were injected with a 10-μl Hamilton syringe.

Melting points. Melting points for the compounds (in fractions IVa–IVf) and their picric acid derivatives were determined with the aid of a Kofler hot-stage microscope. The temperatures obtained are temperatures of equilibrium. The temperature intervals state the limits within which all crystals melted.

RESULTS

Tables I and II show that the relative retention times and melting points of A_1, A_2, B_1 and C agree well with the values given for the corresponding alkylphenanthrenes in reference works. In addition, when A_1, A_2, B_1 and C were each chromatographed together with an authentic sample of the corresponding alkylphenanthrenes, the peaks coincided.

It was not possible to determine the melting point of B_2 because the amount obtained was too small, and as no retention data were available from reference works, B_2 was identified by direct comparison with authentic samples in the gas chromatograph. This test showed that the peaks of B_2 and 9,10-dihydroretene coincided.

The melting point of the retene picrate was determined as 128·3–128·9° which is, rather surprisingly, somewhat higher than the value of 123–124°[11] and 126°[12] indicated in the literature. The melting point of the picrate was checked in a Perkin–Elmer D.T.A. apparatus and a sharp peak indicating the melting point was obtained at 128°. No other changes occurred in the picrate when the temperature was increased at 8°/min from 100° to 140°.

TABLE I.—RELATIVE RETENTION TIMES

Peak	Alkylphenanthrene for comparison*	Column phases and temperatures		
		SE–30 240°C	QF–1 215°C	NPGS 225°C
	Phenanthrene	1·00	1·00	1·00
A_1		1·52	1·50	1·51
	1-Methylphenanthrene	1·52	1·50	1·51
A_2		1·85	1·80	1·72
	2-Ethylphenanthrene	1·89	1·80	1·73
B_1		2·11	2·13	2·06
	1,7-Dimethylphenanthrene	2·13	2·14	2·05
B_2		2·45	1·60	1·49
	9,10-Dihydroretene	—	—	—
C		2·80	2·73	2·60
	1-Methyl-7-ethylphenanthrene	2·83	2·72	2·59
D		3·33	3·06	2·87
	1-Methyl-7-isopropylphenanthrene	3·33	3·06	2·87
E		3·80	3·55	2·92
	1,3-Dimethyl-7-ethylphenanthrene	3·80	3·66	3·03
F		4·45	4·09	3·27
	1,3-Dimethyl-7-isopropylphenanthrene	4·62	4·15	3·28

* The relative retention times of the alkylphenanthrenes are given by Solo and Pelletier,[1] and all original data for the peaks *A–F* have been recalculated to the quoted temperatures for comparison.

TABLE II.—MELTING POINTS

Compound	Melting point, °C	
	Alkylphenanthrene	Picrate
A_1	121·7–122·2	137–138
1-Methylphenanthrene	122·0–122·5[6]	139[6]
A_2	65·0–65·5	95·0–95·5
2-Ethylphenanthrene	65·0–65·5[7]	94·5[8]
B_1	82·5–83·0	131–132
1,7-Dimethylphenanthrene	85–86[9]	132[9]
C	92·5–93·0	135·5–136·5*
1-Methyl-7-ethylphenanthrene	87·5[10]	134[10]*
D	101·0–101·5	128·3–128·8
1-Methyl-7-isopropylphenanthrene	100·5–101·0[11]	123–124[11], 126[12]

* Derivative with 1,3,5-trinitrobenzene.

The relative retention times of peak *E* correspond to those of 1,3-dimethyl-7-ethylphenanthrene. An attempt to determine the melting point of fraction IVe gave a melting range between 65° and 75°. Mass spectrometric analysis of fraction *E* was carried out at Karolinska Institutet, Stockholm, by Dr. R. Ryhage. It showed that the presence of compounds with molecular weights 234 and 248. No authentic sample of 1,3-dimethyl-7-ethylphenanthrene was available.

The relative retention times of peak *F* correspond to those of 3-methylretene. The determination of the melting point gave 35–45°, while Jacobs and Craig[13] state 70–72° for 3-methylretene. The melting point of the picrate was 132–136°; Jacobs and Craig[13] give 143–144°. In column 7 fraction IVf separated into two peaks of about the same size. When an attempt was made to increase the amount injected in this column, in order to get enough material for the determination of the melting point, the separation was reduced considerably and no improved melting point was obtained. No authentic sample of 3-methylretene was available. Fraction IVf was analysed by mass spectroscopy and the results indicated that fraction contained compounds with molecular weights 248, 262, 274 and 288.

Acknowledgements—The author wishes to thank Professor K. J. Karrman for valuable ideas and his interest in this work. Thanks are also due to Dr. L. Haraldson for interesting discussions.

Zusammenfassung—Verschiedene Trennmethoden, besonders die Gaschromatographie, wurden auf Reten aus Kiefernholzteer angewandt. Die relativen Retentionszeiten auf drei verschiedenen Säulen sowie die Schmelzpunkte dienten zur Identifikation der folgenden Verbindungen neben Reten selbst: 1-Methylphenanthren, 2-Äthylphenanthren, 1,7-Dimethylphenanthren, 1-Methyl-7-äthylphenanthren, 9,10-Dihydroreten und möglicherweise 1,3-Dimethyl-7-äthylphenanthren sowie 1,3-Dimethyl-7-isopropylphenanthren. Alle Substanzen bildeten am Auslaß des Gaschromatographen Aerosole. Zur Koagulation dieser Aerosole erwies sich feinste Glaswolle als ausgezeichnet geeignet.

Résumé—On a appliqué différentes méthodes de séparation, spécialement la chromatographie en phase vapeur, au rétène brut obtenu du goudron de bois de pin. Les temps de rétention relatifs sur trois colonnes différentes et les points de fusion ont été utilisés pour identifier les composés suivants à côté du rétène lui-même: 1-méthylphénanthrène, 2-éthylphénanthrène, 1,7-diméthylphénanthrène, 1-méthyl 7-éthylphénanthrène, 9,10-dihydrorétène et probablement les 1,3-diméthyl 7-éthylphénanthrène et 1,3-diméthyl 7-isopropylphénanthrène. Toutes ces substances forment des aérosols à la sortie du chromatographe en phase vapeur. On a trouvé que la laine de verre surfine est un excellent moyen de coagulation de ces aérosols.

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REPLACEMENT SUBSTOICHIOMETRY AND ITS APPLICATION IN ACTIVATION ANALYSIS

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Summary—A new method based on the substoichiometry principle has been developed. Instead of substoichiometric amounts of chelating agent, substoichiometric amounts of aqueous solution of a competing metal are used. Theoretical relationships have been derived for this method of substoichiometric replacement. Possibilities for its application are discussed.

SEPARATION methods in radiochemical analysis, especially in activation and isotope dilution analysis, have been significantly simplified by using the principle of substoichiometry,[1,2] which avoids the necessity of determining the chemical yield of the separation. A still greater advantage of substoichiometry lies in the fact that the selectivity is substantially increased.

The conditions of substoichiometric separation by solvent extraction have been theoretically derived by the authors of this principle—Růžička and Starý.[1,2] They started from the reaction:

$$M + m(HA)_{org} \rightleftharpoons (MA_m)_{org} + mH \tag{1}$$

where the subscript "org" denotes the organic phase. Here and elsewhere, charges are omitted for simplicity. Reagent HA is added in smaller amounts than those stoichiometrically corresponding to the quantity of metal M present. The relationship for the value of the threshold pH of the separation was derived, assuming that more than 99·9% of the organic reagent was used to form the complex MA_m. The relationship for the selectivity of the separation was also derived.

Substoichiometric separation carried out in this way is very advantageous for elements having high values for their extraction constants, but is not very suitable for the determination of metals having low extraction constants, because all metals with higher extraction constants will interfere. For this reason we tried to find a substoichiometric procedure suitable for these elements as well.

On the basis of the same considerations as those of Růžička and Starý we can derive similar relationships for substoichiometric replacement, and consider substoichiometry somewhat more generally. The idea of a "reagent", added in substoichiometric amounts as regards the metal determined, is relative. Let us consider the use of the substoichiometry principle for exchange reactions of the following kind:

$$nMA_m + mN \rightleftharpoons mNA_n + nM \tag{2}$$

where M and N are cations with charges $m+$ and $n+$ respectively, and A is the univalent anion of a chelating agent. Two cases are possible: either a substoichiometric amount of the chelate MA_m is added for the determination of metal N, or a substoichiometric amount of an aqueous solution of metal N is added for the determination of metal M. In the former case the radioactivity of the organic phase is measured, and in the latter, that of the aqueous phase.

The former case has already been applied[3,4] in cases where solutions of metal chelate in the organic phase were found to be more stable towards decomposition than the organic reagent solution HA itself.

In the present paper we shall deal with the second case, *i.e.*, addition of a substoichiometric amount of replacing metal N.

THEORETICAL

Consider the following equilibrium:

$$n(MA_m)_{org} + mN \rightleftharpoons m(NA_n)_{org} + nM. \tag{3}$$

In this case the metal M is displaced into the aqueous phase from the solution of the chelate MA_m in the organic phase by addition of a substoichiometric amount of aqueous solution of the metal N.

The equilibrium (or exchange) constant of reaction (3) is

$$K_e = \frac{[M]^n[NA_n]^m_{org}}{[MA_m]^n_{org}[N]^m}. \tag{4}$$

The extraction constants of both reacting metals are determined from the relationships:

$$K_M = \frac{[MA_m]_{org}[H]^m}{[HA]^m_{org}[M]}; \quad K_N = \frac{[NA_n]_{org}[H]^n}{[N][HA]^n_{org}} \tag{5}$$

where $[HA]_{org}$ denotes the equilibrium concentration of organic reagent in the organic phase.

After introducing equations (5) into equation (4) we obtain:

$$K_e = \frac{K_N{}^m}{K_M{}^n}. \tag{6}$$

By substituting the equilibrium concentrations [M], $[NA_n]_{org}$ and [N] into equation (4) we may derive the condition for the substoichiometric separation of metal M in accordance with reaction (3).

The equilibrium concentration $[NA_n]_{org}$ is derived on the assumption that more than 99·9% of the reagent N is used to form the complex NA_n, *i.e.*,

$$[NA_n]_{org} \cdot V_{org} \geqslant 0{\cdot}999\, c_N \cdot V \tag{7}$$

where V_{org} and V are the volumes of the organic and aqueous phases respectively and c_N is the original concentration of N in the aqueous phase. This condition ensures that the same amount of metal M is always isolated by reaction (3) with a relative error less than 0·1%, *i.e.*, with the accuracy of current analytical methods.

The equilibrium concentration of the chelate, $[MA_m]_{org}$, is determined from the relationship

$$[MA_m]_{org} \cdot V_{org}/m = c_{MA_m} \cdot V_{org}/m - c_N \cdot V/n \tag{8}$$

where c_{MA_m} denotes the original concentration of MA_m in the organic phase.

For the equilibrium concentration of metal N in the aqueous phase, the following expression must apply:

$$[\mathrm{N}]\cdot V = 0{\cdot}001\, c_{\mathrm{N}} V. \tag{9}$$

By solving equations (4)–(9) we obtain the expression:

$$m\log K_{\mathrm{N}} - n\log K_{\mathrm{M}} \geqslant m\log (c_{\mathrm{N}} V/V_{\mathrm{org}}) - n\log\{(c_{\mathrm{MA_m}} - c_{\mathrm{N}} mV/nV_{\mathrm{org}})/[\mathrm{M}]\} - m\log (0{\cdot}001\, c_{\mathrm{N}}). \tag{10}$$

However, having an excess of chelate MA_m present in the organic phase (with respect to the quantity of N added), we must also consider a possible release of M by the reaction

$$(\mathrm{MA_m})_{\mathrm{org}} + m\mathrm{H} \rightleftharpoons \mathrm{M} + m(\mathrm{HA})_{\mathrm{org}} \tag{11}$$

with equilibrium constant

$$K_{\mathrm{M}}' = \frac{[\mathrm{M}][\mathrm{HA}]^m_{\mathrm{org}}}{[\mathrm{MA_m}]_{\mathrm{org}}[\mathrm{H}]^m} = \frac{1}{K_{\mathrm{M}}}. \tag{12}$$

To prevent such a release (which is a replacement side-reaction with protons) the following condition must be fulfilled:

$$[\mathrm{HA}]_{\mathrm{org}}\cdot V_{\mathrm{org}} \leqslant 0{\cdot}001\, c_{\mathrm{MA_m}} V_{\mathrm{org}}. \tag{13}$$

That is to say, the metal chelate in question must be stable at the pH used.

From equations (8), (12) and (13) we obtain for the value of the threshold pH:

$$\mathrm{p}H \geqslant \frac{1}{m} \log \{(c_{\mathrm{MA_m}} - c_{\mathrm{N}} mV/nV_{\mathrm{org}})/[\mathrm{M}]\} - \frac{1}{m} \log K_{\mathrm{M}} - \log 0{\cdot}001 c_{\mathrm{MA_m}} \tag{14}$$

which is the same as that given by Růžička and Starý.[1,2] Equation (14) is fulfilled only for the condition $\mathrm{pH} \leqslant \mathrm{p}K_{\mathrm{HA}} + \log(V_{\mathrm{org}}/V)$, where K_{HA} is the dissociation constant and P_{HA} the distribution coefficient of the organic reagent. Moreover, for replacement substoichiometry the conditions (10) and (14) must both be fulfilled.

It follows from an analysis of equations (10) and (14) that the second term on the right-hand side of the former and the first on the right-hand side of the later can be neglected, as the other terms are of far greater importance. In activation analysis we work with approximately $10^{-3}M$ solutions. If V equals V_{org}, equations (10) and (14) are simplified:

$$m\log K_{\mathrm{N}} - n\log K_{\mathrm{M}} \geqslant 3m \tag{15}$$

$$\mathrm{pH} \geqslant 6 - \frac{1}{m} \log K_{\mathrm{M}}. \tag{16}$$

From the known values of extraction constants and by means of equations (15) and (16) we can predict whether substoichiometric replacement is possible, and over what pH-range.

In practice, however, we must consider that metal ions in the aqueous phase are not in the form of free cations, but may be subject to hydrolysis and formation of complexes with complexing agents present in the solution. This can be dealt with by introducing Ringbom's α-coefficient,[5] defined by the expression $\alpha_M = [M']/[M]$ where $[M']$ is the total concentration of metal M in the aqueous phase and $[M]$ is the concentration of free cations of the metal. The coefficient α_M when a complexing agent is present can be computed from the relationship

$$\alpha_{M(B)} = 1 + \beta_1[B] + \beta_2[B]^2 + \ldots + \beta_m[B]^m \tag{17}$$

where $\beta_1, \beta_2 \ldots . \beta_m$ are the overall stability constants of successive metal complexes with reagent H_nB and $[B]$ is the equilibrium concentration of the anion of the complexing agent at the pH used. The α-values for various metals, complexing agents and pH-values are tabulated.[5] When a complexing agent is present we must use the conditional extraction constants[5] in equation (5):

$$K_M'' = \frac{K_M}{\alpha_M} = \frac{[MA_m]_{org}[H]^m}{[M'][HA]^m_{org}}\ ; \quad K_N'' = \frac{K_N}{\alpha_N} = \frac{[NA_n]_{org}[H]^n}{[N'][HA]^n_{org}}\,. \tag{18}$$

Substituting equations (18) in equation (15) we obtain a general condition for substoichiometric replacement:

$$m \log \frac{K_N}{\alpha_N} - n \log \frac{K_M}{\alpha_M} \geqslant 3m. \tag{19}$$

Analogously, on substituting in equation (16) and considering the dissociation of the organic reagent HA in the aqueous phase, we obtain the relationship for the value of threshold pH:

$$\mathrm{pH} \geqslant 6 - \frac{1}{m} \log \frac{K_M}{\alpha_M} + \log \left(1 + \frac{1}{P_{HA}} + \frac{K_{HA}}{P_{HA}[H]}\right). \tag{20}$$

So far we have considered that only chelate MA_m is present in the organic phase. In general, the organic phase will also contain chelates of other metals extractable under the given conditions. Even in this case a selective separation of metal M can be worked out, but free reagent HA must not be present in the organic phase.

The ratio of the concentrations $[M']$ and $[P']$ of two metals replaced from the chelates MA_m and PA_p by reagent N can be calculated from the following relationship:

$$\frac{[M']}{[P']} = \left(\frac{K_N}{\alpha_N}\right)^{(n-p)/n} \cdot \frac{K_P}{\alpha_P} \cdot \frac{\alpha_M}{K_M} \cdot \left(\frac{[N]}{[NA_n]_{org}}\right)^{(m-p)/n} \cdot \frac{[MA_m]_{org}}{[PA_p]_{org}}\,. \tag{21}$$

In this case the presence of complexing agents in the aqueous solution of reagent N is already taken into consideration, $[M']$ and $[P']$ being the total concentrations of metal M and metal P species in the aqueous phase.

In stoichiometric separation, the selectivity of the separation of two metals is greater than in separation with an excess of reagent. Consider a simple case where the organic phase contains equal concentrations of chelates MA_m and PA_p, and suppose $m = p = z$; we want to obtain quantitative separation of metal M from metal P by means of an excess of N, *i.e.*, to reach a state where $[MA_z]_{org}/[PA_z]_{org} < 0{\cdot}01$ and $[M']/[P'] > 100$, which requires that the ratio $K_p\alpha_M/\alpha_P K_M$ should be greater than 10^4 and hence that the pH and the concentration of N have to be accurately maintained. With substoichiometric separation, by using an amount of N corresponding to half the quantity of M present, the same result can be achieved (*i.e.*, $[M']/[P'] > 100$) even if the value of $K_p\alpha_M/\alpha_P K_M$ is as low as 200, because $[MA_z]_{org}/[PA_z]_{org}$ is then 0·5. In this case, the selectivity of substoichiometric separation does not depend on the choice of the replacing metal N, provided that conditions (19) and (20) are fulfilled.

On the basis of the known values of extraction constants and α-coefficients the most suitable conditions (pH, masking agent, *etc.*) for a selective separation of a number of metals may be chosen with the aid of relationships (19), (20) and (21).

We have assumed that no free organic reagent HA is present in the organic phase. This condition may be fulfilled by extracting a group of metals by reagent HA into the organic phase and stripping excess of HA from the organic phase by washing with water adjusted to a pH greater than $pK_{HA} + \log P_{HA} + \log V_{org}/V$. Metals forming extractable chelates that are unstable at this pH are also decomposed and stripped. Then the chelates remaining in the organic phase can be replaced by a substoichiometric amount of N. Alternatively, the presence of free organic reagent HA can sometimes be avoided by using a substoichiometric amount of it for the initial extraction. Another possibility is the chemical destruction of the free reagent, as it is often less stable than its metal chelates.

APPLICATION

Some practical consequences of the theoretical relationships may be shown in the case of the dithizonates and diethyldithiocarbamates of heavy metals.

The extraction constants of dithizonates and dissociation constants and distribution coefficients of the reagents used in the calculations are taken from Starý's monograph.[6] The values of the extraction constants of mercury and copper diethyldithiocarbamates are taken from Kratzer's work[7] ($\log K_{Hg} = 31{\cdot}9$ and $\log K_{Cu} = 13{\cdot}7$ for carbon tetrachloride). The α-coefficients are calculated from the stability constants[8] by means of equation (17).

It follows from equations (14) and (20) that the lower $[MA_m]_{org}$ is, the narrower is the pH range of substoichiometric replacement. This is shown in Fig. 1 in the case of replacement of indium from its dithizonate in chloroform solution by amounts of mercury(II) equivalent to 50% of the amount of indium dithizonate. The pH ranges observed agree in general with those predicted from equations (14) and (20)—the theoretical pH range for $3{\cdot}3 \times 10^{-4}M$ indium dithizonate in chloroform is 7–9. Good reproducibility of substoichiometric replacement separation with that concentration of indium dithizonate has been proved experimentally, Fig. 2.

It follows from the values of the extraction constants that copper is replaced from copper(II) diethyldithiocarbamate $[Cu(DDC)_2]$ by mercury(II). On the other hand, in the presence of iodide (which forms a very strong tetraiodomercurate(II) complex,[8] $\log K = 29{\cdot}8$) it is possible to replace mercury from mercury(II) diethyldithiocarbamate $[Hg(DDC)_2]$ by copper. The pH-dependence of this substoichiometric replacement is shown in Fig. 3 for an amount of copper equivalent to 50% of the mercury(II) diethyldithiocarbamate.

The experimentally determined pH range was 4·5–10·5, which is in accordance with the range 5–11 calculated from the relationships (14), (19) and (20).

The curve in Fig. 3 shows that in more acidic systems the replacement of mercury is limited by the instability of the excess of $Hg(DDC)_2$ in the organic phase [equations (14) and (20)], and in alkaline media by the relative weakness of $Cu(DDC)_2$ [equation (19)], so that at high pH copper does not replace mercury even in the presence of iodide. The reproducibility of this separation (at pH 6) is shown in Fig. 4.

The method of substoichiometric replacement has been used in practice for the determination of the traces of thallium by activation analysis.[9]

CONCLUSION

In this paper theoretical relationships for substoichiometric replacement have been derived. The possibility of the formation of several extractable complexes of a given metal has not been considered—in such cases the relationships derived would be more complicated and so would all the theory. Fortunately this case occurs but

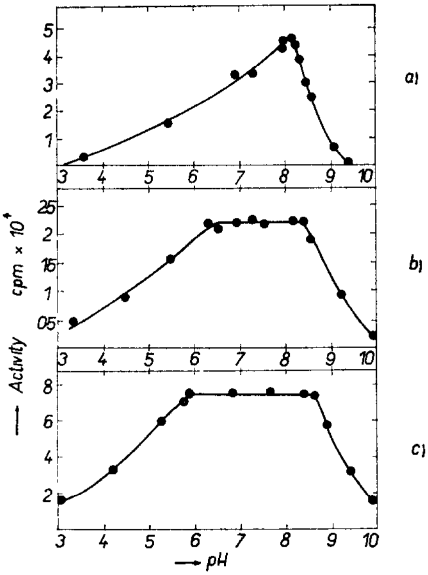

FIG. 1.—Effect of pH on substoichiometric replacement of indium from In-dithizonate by mercury(II).

Substoichiometric amounts (50%) of Hg^{2+} were added. Activity of the aqueous phase (^{114m}In) was measured. The horizontal part of the curves corresponds to 50% of the total activity of ^{114m}In. Shaking time 40 secs. $V = V_{org} = 10$ ml. Concentrations of In-dithizonate in CHCl$_3$: *a*—3·3 × 10^{-6}*M*; *b*—3·3 × 10^{-5}*M*; *c*—3·3 × 10^{-4}*M*.

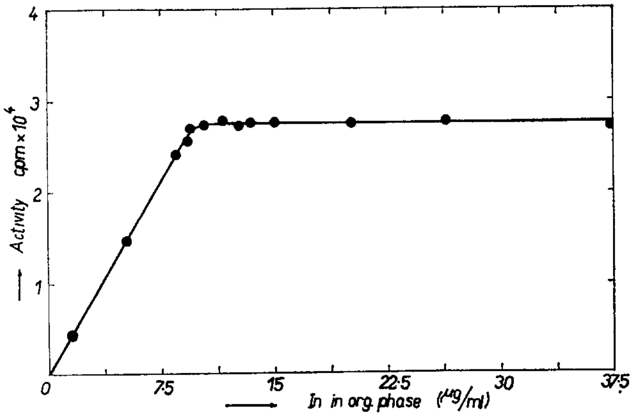

FIG. 2.—Reproducibility of substoichiometric replacement of indium from In-dithizonate by mercury(II).

$V = V_{org} = 10$ ml. Concentration of In in the organic phase was varied and a fixed quantity of Hg (250 µg) added. The pH of the aqueous phase was ~8. Activity of ^{114m}In in the aqueous phase was measured. Shaking time 40 sec.

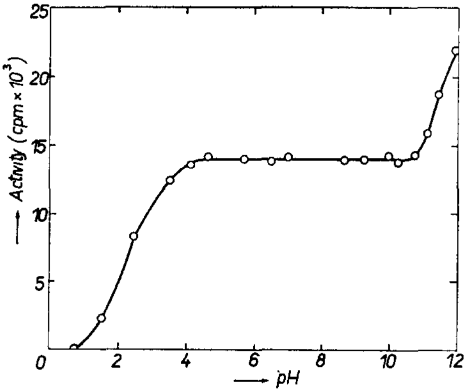

FIG. 3.—Effect of pH on substoichiometric replacement of mercury(II) from Hg-diethyldithiocarbamate by copper(II) in the presence of iodide. Substoichiometric amounts (50%) of Cu^{2+} were added. Activity of the organic phase (^{203}Hg) was measured. The horizontal part of the curve corresponds to 50% of the total activity of ^{203}Hg. $Hg(DDC)_2$ $1 \times 10^{-4}M$ in CCl_4; 0·1M KI. Shaking time 10 min. $V = V_{org} = 10$ ml.

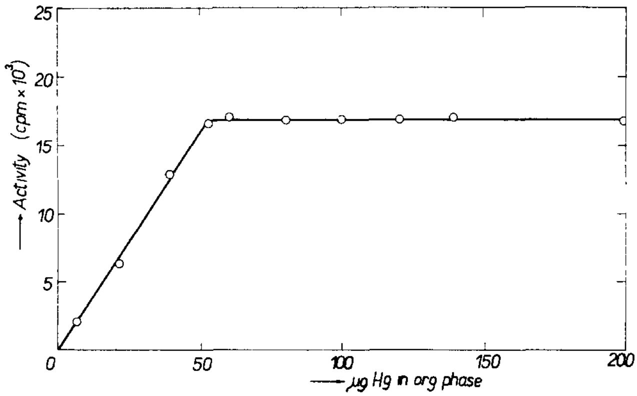

FIG. 4.—Reproducibility of substoichiometric replacement of mercury from Hg-diethyldithiocarbamate by copper(II) in the presence of iodide. $V = V_{org} = 10$ ml. Concentration of Hg in organic phase was varied and a fixed quantity of Cu (16 µg) added. Activity of ^{203}Hg in the aqueous phase was measured. The pH of the aqueous phase was ~6; 0·1M KI. Shaking time 10 min.

seldom with the majority of the common chelating extracting agents (though some metals form secondary dithizonates with dithizone at higher pH-values).

Substoichiometric replacement can be used even in cases where the usual substoichiometric separation is not sufficiently selective. After some modifications it will be possible to apply replacement substoichiometry to separation procedures other than extraction and perhaps in other methods than activation analysis, *e.g.*, in isotope dilution analysis.

Acknowledgements—The authors would like to express their thanks to Dr. M. Křivánek, Dr. M. Kyrš and Dr. V. Knobloch for their critical discussion and for their interest in this work.

Résumé—On a élaboré une nouvelle méthode basée sur le principe de la substoechiométrie. Au lieu de quantités substoechiométriques d'agent chélatant, on utilise des quantités substoechiométriques de solution aqueuse d'un métal entrant en réaction. On a calculé des relations théoriques pour cette méthode de remplacement substoechiométrique. On discute des possibilités d'application.

Zusammenfassung—Eine neue auf dem substöchiometrischen Prinzip beruhende Analysenmethode wurde entwickelt. Statt unterstöchiometrischen Mengen von Chelatbildner werden unterstöchiometrische Mengen wäßriger Lösung eines konkurrierenden Metalls verwendet. Für dieses Verfahren unterstöchiometrischer Verdrängung wurden theoretische Beziehungen abgeleitet. Anwendungsmöglichkeiten werden diskutiert.

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SPECTROSCOPY IN SEPARATED FLAMES—III*

USE OF THE SEPARATED NITROUS OXIDE-ACETYLENE FLAME IN THERMAL EMISSION SPECTROSCOPY

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Summary—The separation of a premixed nitrous oxide–acetylene flame at a modified commercial burner is described. The reducing interconal zone of the fuel-rich separated flame exhibits low radiative background. The reducing atmosphere and high temperature of this flame result in an effective medium for the excitation of the atomic line spectra of the refractory elements. The use of the fuel-rich flame in the flame photometry of these elements has been investigated.

In a previous paper in this series we have reported several useful properties of the separated air–acetylene flame in thermal emission spectroscopy.[1] The separation, for example, results in reduction, by several orders of magnitude, of the continuum background radiation due to the reaction $CO + O \rightarrow CO_2 + h\nu$, and almost quantitatively suppresses the background molecular band-emission from OH.

In order to provide high sensitivity in flame emission spectroscopy for elements which have high excitation potentials, or which form stable molecular compounds in most flames of hydrocarbons supported by air, high temperature flames of a reducing nature are required. Fuel-rich oxygen–hydrogen and oxygen–acetylene flames have been used by several workers to meet these requirements.[2,3,4] Because of the high burning velocities of these mixtures, these flames are usually maintained on non-premix burners of the total consumption type. The turbulent flames which result at most burners of this type have several undesirable properties compared with the properties of premixed flames. Thus the flames are generally turbulent and noisy, and exhibit ill-defined reaction zones which result in high background radiation from the flame itself. In addition, atomization in the flames is usually inefficient owing to the introduction of relatively large droplets of the solution aspirated from the direct nebulizer.

Premixed oxy-acetylene and oxy-hydrogen flames are difficult to support owing to their extremely high burning velocities. Fassel and co-workers[5,6] have reported the production of a low background oxy-acetylene flame of this type, however, using a total consumption nebulizer–burner fitted with a short capillary which acts as a mixing chamber for the unburnt gases. Recently, the advantages of the premixed nitrous oxide–acetylene flame have been demonstrated for atomic absorption spectroscopy.[7] This flame attains a high temperature without an excessively high burning velocity. The fuel-rich nitrous oxide–acetylene flame also exhibits the strongly reducing properties necessary to support the existence of free atoms of many elements which form thermally stable oxides. The premixed nitrous oxide–acetylene flame, therefore, would appear also to possess considerable potential for emission flame spectroscopy.

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* Part II: *Talanta*, 1968, **15**, 199.

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Owing to its high temperature the flame shows intense background emission from the flame species and reactions in the outer mantle (principally from the species OH and the reaction $CO + O \rightarrow CO_2 + h\nu$). Separation of the stoichiometric or slightly fuel-rich nitrous oxide–acetylene flame removes the background emission due to the diffusion zone which surrounds the primary region. Because the flame is protected from ingress of air, the reducing zone of the slightly fuel-rich flame becomes extended in length and provides an "atom reservoir" of high temperature, reducing properties and low radiative background. This paper reports the properties of this separated flame and its analytical application in flame photometry. The present investigation is restricted to those elements which normally form very stable oxides, with the result that their atomic line emission spectra are not generally observed in conventional cooler flames, and which also cannot be determined with great sensitivity by atomic absorption spectroscopy (even in the nitrous oxide–acetylene flame).

EXPERIMENTAL

Apparatus

The burner and separator used in this study are shown in Fig. 1. The burner is based on a Unicam SP 900 emission burner in which the conventional Méker-type burner head is replaced by a stainless

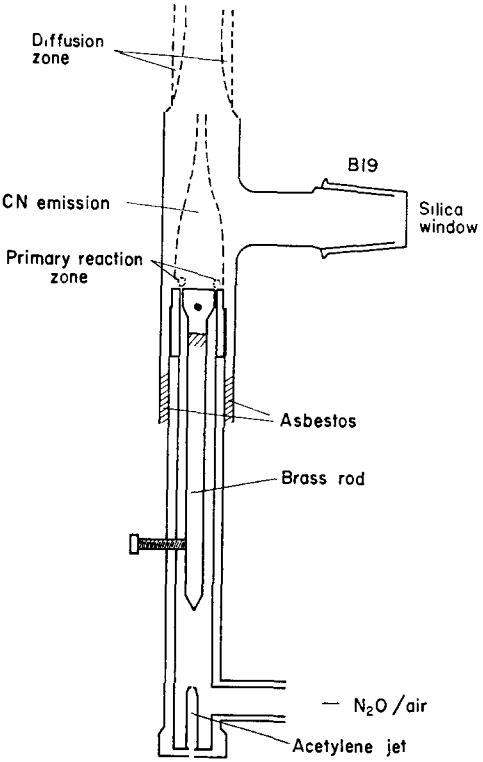

FIG. 1.—Diagram of burner arrangement with silica separator mounted.

steel head with a circular slot 0·50 mm wide and 11 mm internal diameter. The central steel plug of this burner head is threaded internally to take a threaded brass rod. The steel plug is held centrally in position in the burner head by grub screws or steel pins and the brass rod is centred in the burner stem by three brass positioning screws inserted at 120° intervals at the same height through the wall of the burner barrel (only one of these is shown in Fig. 1). The central brass column and brass positioning screws also serve to conduct away heat from the central plug of the burner head. The silica separator tube used is 10 cm in length and 24 mm internal diameter. A short silica side-arm is fused to the separator tube and fitted with a B19 ground-glass cone and socket, to which an optical quality silica end-window is cemented. The silica separator fitted with side-arm and cone was supplied direct by Jencons Ltd., Hemel Hempstead, England.

Air, nitrous oxide and acetylene pressures and flow-rates were controlled by the cylinder reduction valves and rotameters fitted with needle valves. It is necessary to light the flame on an air–acetylene mixture, and gradually to replace the air by nitrous oxide *via* an arrangement of a T-piece and two rotameters. The acetylene flow-rate may then be adjusted to produce a separated slightly fuel-rich flame with a well developed red interconal zone. A nitrous oxide flow-rate >5 l./min was always used in order to avoid any possibility of blowing back of the flame.

The spectral emission from the flame species, and the atomic and molecular emission from elements introduced into the flame were examined and identified, with the burner mounted on the optical bench of a Hilger Large Quartz Spectrograph. The quantitative flame photometric examination, establishment of spectral line intensities, detection limits and recordings of flame spectra were made with a Unicam SP 900A flame spectrophotometer fitted with a 0–10 mV Honeywell strip chart recorder. For work at higher resolution the burner was mounted on the optical bar of a Techtron AA4 atomic absorption spectrophotometer. The atomic and molecular emission from the separated flame was modulated by a Techtron flame chopper (285 cps) and viewed by the monochromator and a.c. detector system of the apparatus. This spectrophotometer was fitted with a spectrum scanning motor (10 Å/min) and Sargent recorder. Thus in both spectrophotometers the burner arrangement employed replaced the conventional burner unit fitted to the commercial flame spectrophotometer unit. The indirect nebulizers of both instruments were retained and sample solutions were aspirated with nitrous oxide. All measurements were made with the observation window of the separator placed directly in front of the entrance slits, and in the case of the Techtron instrument the modulating chopper was positioned between the slit and the observation window.

RESULTS AND DISCUSSION

Flame emission characteristics

When the flame is lit, the primary reaction zone of the premixed separated flame adopts a shallow conical form at the slot of the burner head. The diffusion zone, where the hot reaction products of the primary combustion burn with support from surrounding air, is maintained at the top of the separator tube. The interconal zone of the flame, opposite the observation window, is virtually radiationless for a stoichiometric flame ($C_2H_2 + 2N_2O$). The interconal zone of fuel-lean flames, however, exhibits some OH background radiation and continuum owing to the reaction of the carbon monoxide with the excess of oxygen. Slightly fuel-rich flames exhibit intense emission from the CN red and violet band systems (the 'red-feather' of atomic absorption flames). In the unsheathed type of flame commonly used in atomic absorption spectroscopy of the refractory elements, the reducing zone is restricted owing to the ingress of air from the surroundings. In contrast to this, the reducing CN zone in the separated flame extends well above the top of the separator, although the CN emission is most intense in the hottest part of the flame immediately above the primary zone. When the mixture strength exceeds *ca.* 1·1 in rich flames, the excess of carbon provided by the fuel is not utilized in the reaction in the primary zone to form CN, and the flame then becomes luminous owing to the formation of solid carbon.

The observation side-arm and window were positioned vertically to view the area just above the primary zone and to avoid interference from the intense radiation which it emits. Figure 2 shows the recorded flame spectrum from this part of the slightly fuel-rich flame, obtained with the Unicam spectrophotometer. This exhibits emission from molecular band systems of C_2, CH, NH and CN, the principal feature being the intense emission from the CN violet sequences, of which the most intense band heads occur at 3883·4 Å (0,0), 3590·4 Å (1,0) and 4216·0 Å (0,1).

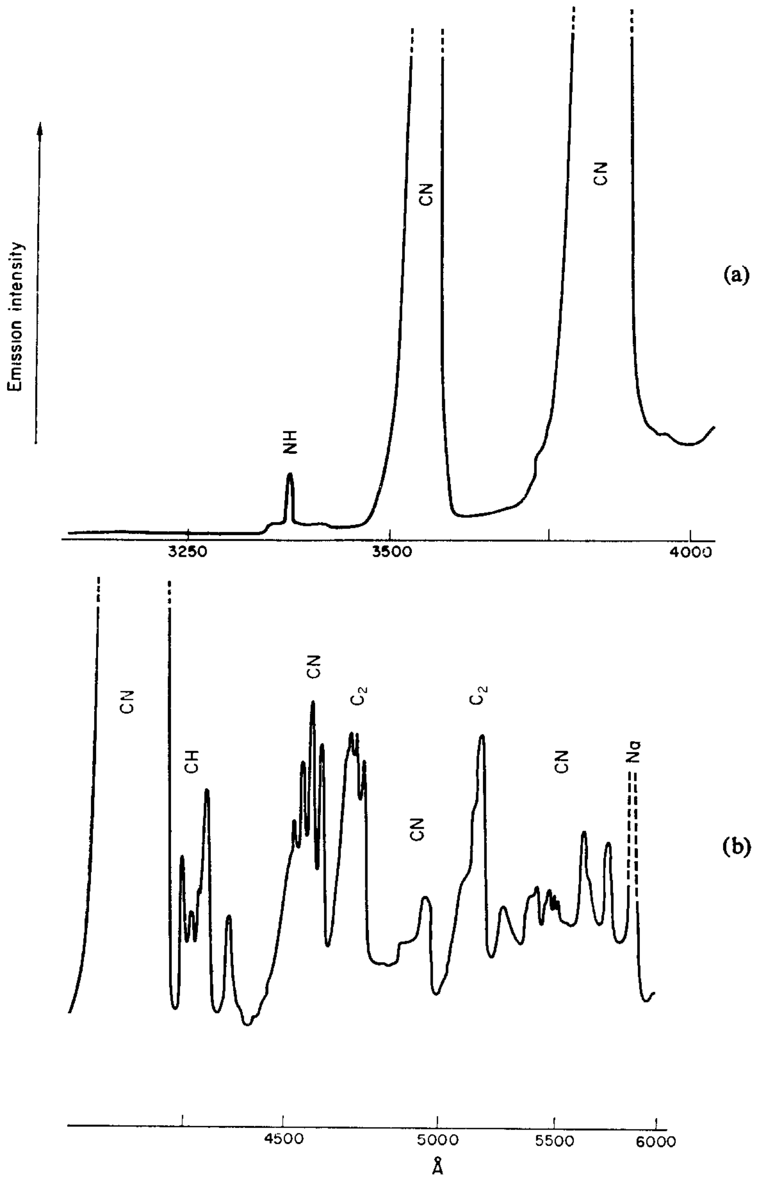

FIG. 2.—Background emission spectrum of separated fuel-rich flame (recorded with prism spectrometer).

The flame background is otherwise very low in the visible region above 4200 Å and extremely low in the ultraviolet part of the spectrum. The OH band emission, which is so troublesome between 2811 Å and 3200 Å in the emission spectroscopy of many elements in conventional flames, is almost quantitatively suppressed. The background chemiluminescence continuum from the reaction $CO + O \rightarrow CO_2 + h\nu$ is also absent in the interconal zone of the separated flame. The cause of this suppression of the OH and CO + O background is the absence of excess of OH or oxygen in this zone of the fuel-rich flame. Further oxidation of the interconal gases to produce this background can only occur at the top of the separator tube in the diffusion zone. When the Techtron AA4 grating monochromator is used, its high resolution (33 Å/mm) ensures that only at wavelengths near the three violet CN-sequences is the flame background significant.

A comparison of the background emission of the separated flame and a similar unseparated conventional flame at the same burner showed that separation resulted in reduction by a factor of 15 in the CO + O continuum background at 4000 Å. The reduction factor in the OH background radiation between 3064 and 3200 Å was approximately 500. The suppression of the background emission in this region is particularly important because aluminium, molybdenum, titanium and vanadium all have important resonances lines in the region 3080–3200 Å. Figure 3 illustrates this, and compares the background emission intensity from an unseparated flame with the emission spectrum from the interconal part of the fuel-rich separated flame when a 100-ppm molybdenum solution is aspirated. It is not possible to show these

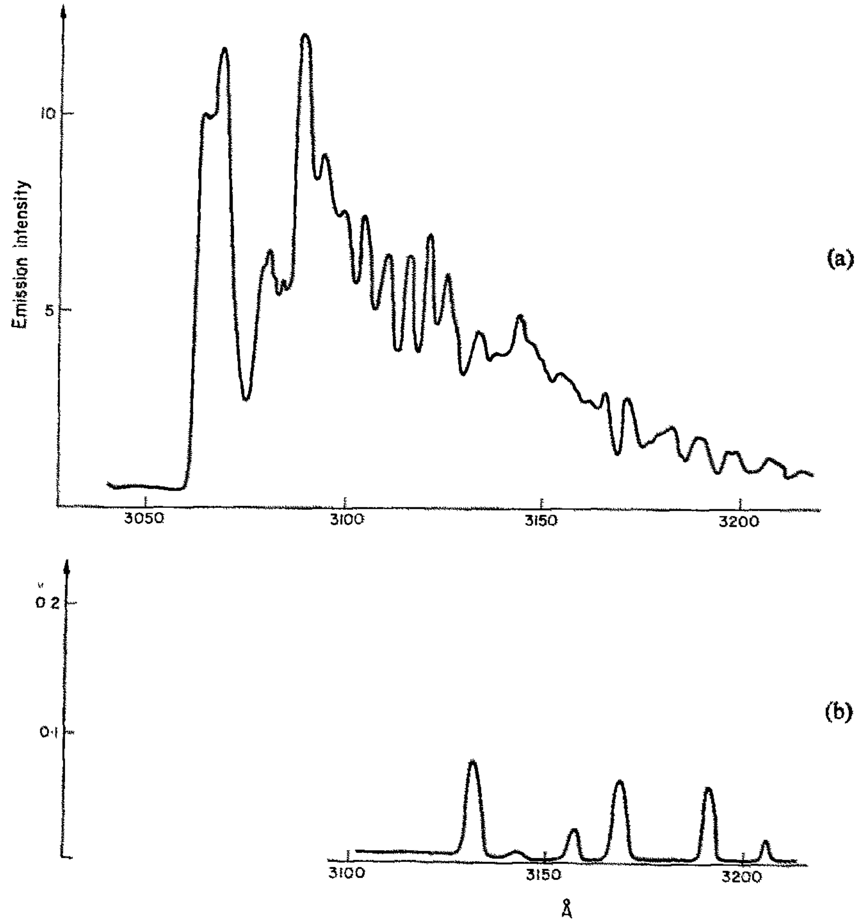

FIG. 3.—(*a*) Background emission from OH in unseparated N_2O–C_2H_2 flame between 3050 and 3200 Å.
(*b*) Emission spectrum from separated fuel-rich N_2O–C_2H_2 flame in same region under same conditions; 100 ppm molybdenum solution sprayed.

two spectra on the same intensity scale, owing to the intense emission from the unseparated flame in this region. Without the flame separator it would be practically impossible to observe atomic emission in this region of the spectrum, except for concentrated solutions and with extremely high resolution spectrometers.

In addition to the suppression of the OH and CO + O continuum background, we have found that the absolute intensity of the band emission due to CN increases in the separated flame relative to the CN emission from the unseparated flame. This appears to be a direct result of the protection of the reducing interconal zone from atmospheric oxygen. We have also observed an increase in emission for the atomic emission from the refractory elements introduced into the fuel-rich separated flame, relative to their emission in the conventional flame. This increased atomic emission occurs in spite of the fact that the separated nitrous oxide–acetylene flame, like the separated air–acetylene flame reported earlier,[1] must inevitably be slightly cooler than the unseparated flame. It is possible that the reducing protected interconal zone of the separated nitrous oxide–acetylene flame supports the ground state population of free atoms of elements which form refractory oxides more efficiently than the unseparated flame.

The unique reducing properties of the separated fuel-rich nitrous oxide acetylene flame are due to the high concentration of CN in the interconal zone and the high flame temperature. The reducing effect can be illustrated in the separated flame by studying visually the effect of varying the nitrous oxide–acetylene mixture strength when concentrated solutions ($0{\cdot}1M$) of elements which form refractory oxides are introduced into the flame. Vanadium, titanium and aluminium monoxides are normally formed and exhibit well-known molecular band spectra in most flames.[8] Emission from these same species is also observed in the lean and stoichiometric nitrous oxides–acetylene separated flames in the interconal zone, especially with vanadium and titanium which show intense yellow-green and yellow emission respectively. When the acetylene flow-rate is increased to produce a fuel-rich flame this emission gradually disappears from the interconal space and atomic V and Ti line emission takes its place. Emission from VO and TiO can then be observed at the tip of the violet-red reducing zone where it merges with the secondary diffusion zone. Molybdenum produces a green continuum emission in lean and stoichiometric flames, attributable to higher oxides of molybdenum. When molybdenum is introduced into the fuel-rich flame, however, the whole interconal zone exhibits an intense orange-red emission. This emission is so intense that it completely masks the CN red visible emission. The species responsible for this emission is MoO, the emission from which in flames does not appear to have previously been reported, but has been observed in arcs between molybdenum poles.[9] Figure 4 shows a recording microphotometer tracing (from an Ilford Long Range spectrum plate used in the large quartz spectrograph) of the characteristic red portion of the MoO spectrum in the fuel-rich flame. The wavelengths of the strongest band heads have been assigned.

Elements which do not normally give intense atomic emission in conventional air–acetylene or oxy-hydrogen flames, but which are readily atomized and excited in the reducing fuel-rich nitrous oxide–acetylene flame, include aluminium, beryllium, molybdenum, titanium, vanadium and tungsten. No significant atomic emission has been detected for boron, silicon, niobium, tantalum and uranium. The results

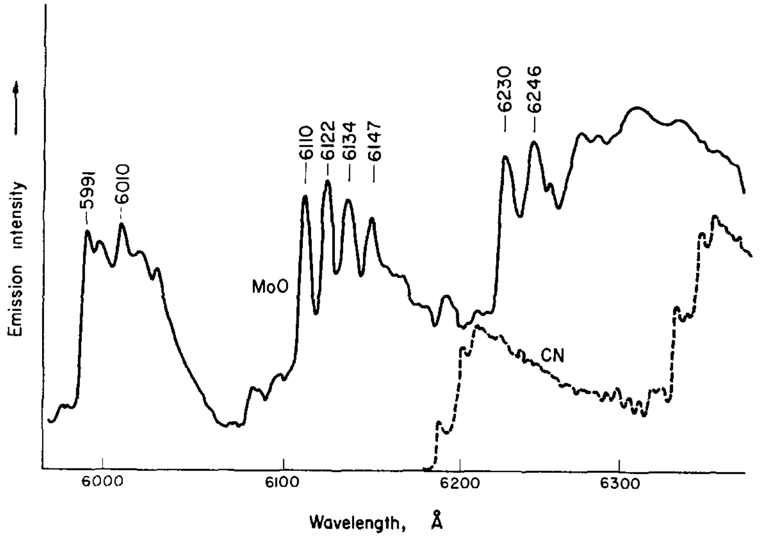

Fig. 4.—Microphotometer recording of characteristic part of band spectrum due to MoO obtained in fuel-rich N_2O–C_2H_2 flame. Dotted line shows spectrum of flame alone (CN red band system) in same region.

Ilford Long Range spectrum plate, Hilger Large Quartz Spectrograph, 50 μ slit, 5 min exposure. Wavelengths of strongest band heads assigned.

of a separate study of the emission from the rare earth elements in this flame are very promising and will form the subject of a later communication. The results for the other elements investigated are summarized in Table I, which gives the relative intensities of the strongest lines and the detection limits for the lines suggested for analytical flame spectrophotometry. Several other lines have also been observed, particularly for vanadium, which emits a very rich spectrum. In cases where the lines are not completely resolved, *e.g.*, for the vanadium 3183·99, 3183·41 and 3185·40 Å triplet, the intensity quoted is the peak intensity obtained with the Techtron spectrophotometer at a slit-width of 100 μ (3·3 Å band-width). The detection limits quoted for the Techtron AA4 arrangement could probably be substantially improved if the modulating chopper were less bulky, so that the flame could be brought closer to the monochromator entrance slit. Under our experimental conditions the flame was about 12 cm from the entrance slit of the monochromator, and the slit views only a small area of the interconal zone of the flame. The light-gathering power of the Unicam SP900A spectrophotometer is much greater, but the resolving power of this instrument is relatively low, particularly in the visible region. The strong Mo line emission at 3902·96 Å, for example, is rather too close to the intense CN band head at 3883·4 Å to allow the use of this line for analysis with this apparatus. For the important ultraviolet region below 3200 Å, however, the resolution of the prism instrument is fully adequate. The detection limits quoted in Table I illustrate the relative performance of the two instruments. When the Al lines at 3944·03 and 3961·53 Å are employed for its determination, some radiation interference from the Ca^+ (3933·67 and 3968·47 Å) ion doublet is experienced when the lower resolution spectrometer is employed. This ionization interference from calcium can, however, be removed by the suppression of ionization by addition of potassium.

TABLE I.—SENSITIVITIES OBTAINED IN SEPARATED NITROUS-OXIDE ACETYLENE FLAME

Element	Line, Å	Relative intensity* (prism spectrometer 100 μ slit)	Detection limit	
			Unicam prism spectrometer, *ppm*	Techtron grating spectrometer (100 μ slit), *ppm*
Aluminium	3961·5	217	0·2	0·1
	3944·0	108	0·5	0·2
	3092·7	17		
	3082·2	8		
Beryllium	2348·6	3	2	0·3
Molybdenum	3864·11	On CN Band		
	3798·3	148		0·5
	3208·8	3		
	3194·0	13	0·5	
	3170·4	14	0·5	
	3158·2	5	1·5	
	3132·6	16	0·5	
	3903·0	100	10	0·2
Titanium	3998·6	40		0·5
	3989·8	30		
	3981·8	26		
	3958·2	33	2	
	3956·3			
	3948·7	20		
	3752·9	24		
	3741·1	17		
	3729·8	13		
	3653·5	27	2	1
	3642·7	27		
	3635·5	23		
Vanadium	4408·5	79		
	4406·1			
	4400·6	9		
	4395·2	21		
	4390·0	40		
	4384·7	64		
	4379·2	86	1	0·5
	3185·4			
	3184·0	28	0·2	0·2
	3183·4			
Tungsten	4008·8	4		20

* Relative to 3903 Å Mo line.

Figure 5 shows the effect of nitrous oxide–acetylene mixture strength on the atomic emission of molybdenum, aluminium and titanium in the internal zone of the separated flame and also shows its effect on the molecular band emission intensity of CN in the same region. The intensity of emission from the atoms of these elements introduced into the flame shows a sharp increase when the mixture becomes fuel-rich and at the same point at which a steady increase in the emission intensity from CN begins to occur. The variation in absorbance due to CN at the 3883 Å head of the (0,0) sequence of CN, as mixture strength in the unseparated flame is altered, has recently been reported, in a separate communication from this laboratory, to show a

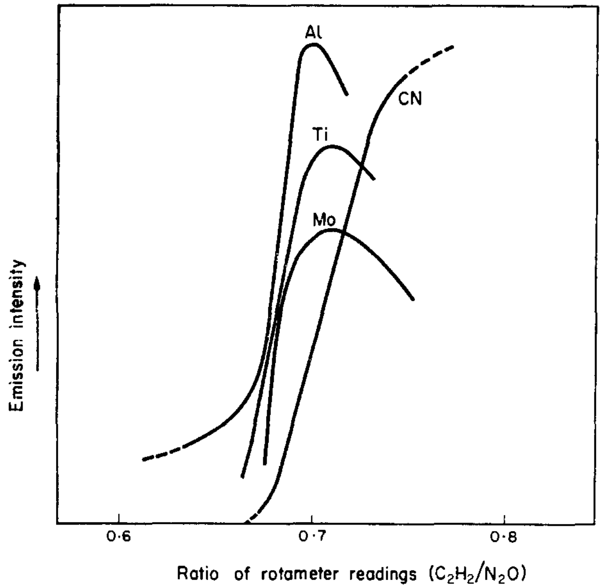

FIG. 5.—Effect of mixture strength on molecular band emission intensity from CN at 3883 Å band and atomic emission from aluminium (3961·5 Å), molybdenum (3194·0 Å) and titanium (3653·5 Å).

similar profile.[10] It appears that the abundance of free atoms of refractory elements in the interconal zone is closely related to the population of CN in this region. The decrease in atomic emission intensity for the elements shown in Fig. 5 when the mixture becomes very fuel-rich may be explained by the slightly cooler nature of the richer flames. Figure 5 also shows that the mixture strength must be carefully controlled in order to obtain good sensitivity and precision when this flame is employed for the flame photometric determination of these elements.

CONCLUSIONS

The sensitivities obtained in thermal emission for the elements investigated in the separated nitrous oxide-acetylene flame compare very favourably indeed with the sensitivities obtainable in atomic absorption spectroscopy at long (5 cm) burners and conventional nitrous oxide-acetylene flames. The high sensitivity obtainable results from the high flame temperature, and the highly reducing nature of the fuel-rich separated flame, combined with its very low background emission. The extended reducing zone makes it easier to optimize the optical arrangement, and, for a given nebulization rate and fuel/oxidant flow-rate ratio, results in a larger total number of emitting atoms in the flame. The results obtained also compare favourably with the reported sensitivities in more conventional hot flames (oxy-hydrogen and oxy-acetylene) at non-premix burners. The low background and intense atomic emission available with this flame permit the use of a monochromator of quite high resolution at narrow slit-width without loss of sensitivity. The narrow band-pass thus obtained confers good selectivity in the flame spectrophotometric determination of the elements investigated and minimizes interference from the atomic or molecular emission of other species present in the flame. The relatively "clean" flame background spectrum also facilitates the use of flame spectra for the qualitative identification of elements present in very dilute solutions introduced into the flame. Owing to the use of a stable premixed flame with low background, the flame noise levels are minimized (especially at the narrow slit-widths used), and good reproducibility is obtained.

Acknowledgement—We are grateful to the Courtauld Research Foundation for a grant for the purchase of apparatus used in this study.

Zusammenfassung—Die Auftrennung einer vorgemischten Lachgas-Acetylen-Flamme an einem modofizierten handelsüblichen Brenner wird beschrieben. Die reduzierende Zone zwischen den Kegeln der aufgetrennten fetten Flamme zeigt geringen Strahlungsuntergrund. Die reduzierende Atmosphäre und die hohe Temperatur dieser Flamme liefern ein wirksames Medium zur Angregung der Atomlinienspektren der feuerfesten Elemente. Die Verwendung der fetten Flamme bei der Flammenphotometrie dieser Elemente wurde untersucht.

Résumé—On décrit la séparation d'une flamme prémélangée protoxyde d'azoteacétylène avec un brûleur commercial modifié. La zone interconique réductrice de la flamme séparée riche en combustible présente un faible fond rayonnant. L'atmosphère réductrice et la haute température de cette flamme ont pour conséquence un milieu efficace pour l'excitation des spectres de raies atomiques des éléments réfractaries. On a étudié l'emploi de la flamme riche en combustible dans la photométrie de flamme de ces éléments.

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FLUORESZENZANALYTISCHE BESTIMMUNG VON SULFIDIONEN IM NANOGRAMMBEREICH

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Zusammenfassung—Zur Bestimmung von Sulfid im Bereich von 1–10 ng/ml wurde eine Methode ausgearbeitet, die auf der Fluoreszenzlöschung einer alkalischen Lösung von Fluorescein-mercuri-acetat (FMA) durch Sulfid oder andere Schwefelverbindungen beruht. Zur Standardisierung wird eine Diphenylthioharnstofflösung verwendet. Die Standardabweichung für die Bestimmung von 3,5 ng/ml Sulfid war 0,17 ng/ml. Die Methode eignet sich zur Bestimmung kleinster Schwefelmengen in organischen Substanzen nach einem hydrierenden Aufschluß.

DIE VORLIEGENDE Arbeit befaßt sich mit der Bestimmung von Sulfidionenkonzentrationen im unteren Nanogrammbereich als Voraussetzung für eine allgemeine Bestimmung sehr kleiner Schwefelmengen.

Von den verschiedenen in der Literatur beschriebenen Prinzipien zur Bestimmung sehr kleiner Sulfidionenkonzentrationen[1–13] wurde das von Wronski[7–10,12] sowie Karush, Klinman und Marks[11] angegebene Verfahren, welches auf der Fluoreszenzlöschung von merkurierten organischen Fluoreszenzfarbstoffen durch Sulfidionen beruht, als besonders leistungsfähig gefunden.

Während die Quecksilberverbindungen von Rhodamin B, α-Naphthol, Morin, Cumarin und Eosin, wie orientierende Versuche zeigten, zu instabil sind und schnell der Hydrolyse unterliegen, eignet sich das Fluorescein-mercuri-acetat (FMA) zur Löschreaktion sehr gut, da nur in dieser Verbindung, wie molekülspektroskopische Untersuchungen und Vergleichsmessungen mit merkuriertem Eosin zeigten, eine C–Hg-Bindung vorliegt. Abbildung 1 gibt das Fluoreszenz-Emissions- und -Anregungsspektrum von FMA in 0,1n Natronlauge wieder. Das Anregungsmaximum liegt bei 499 nm und das Emissionsmaximum bei 520 nm.

Die Fluoreszenz dieser FMA-Lösung zeigt eine starke Abhängigkeit von Konzentration, Acidität, Licht, Temperatur und begleitenden Elementen. Die Einflüsse dieser Faktoren wurden untersucht und lassen sich den Abb. 2–6 entnehmen. Die Fluoreszenzintensität von FMA in 0,1n Natronlauge verläuft im Konzentrationsbereich von 10^{-8} bis 5×10^{-6}m linear.

Abbildung 2 über die Aciditätsabhängigkeit der Fluoreszenzintensität von FMA zeigt, daß nur im alkalischen Bereich, in dem FMA als zweiwertiges Anion vorliegt, Fluoreszenzstrahlung emittiert wird. Innerhalb des alkalischen Bereiches zeigt sich nur eine ganz geringe Abhängigkeit. Es ist also nicht erforderlich, mit stark alkalischen FMA-Lösungen zu arbeiten.

FMA-Lösungen sind sehr lichtempfindlich, sodaß man sie im Dunkeln aufbewahren muß. Die Fluoreszenzintensität einer FMA-Lösung (8 ng FMA/ml) nahm im diffusen Tageslicht in 24 h um 50% ihres Ausgangswertes ab. Im Dunkeln aufbewahrte Lösungen zeigen über mehrere Monate konstante Fluoreszenzintensitäten.

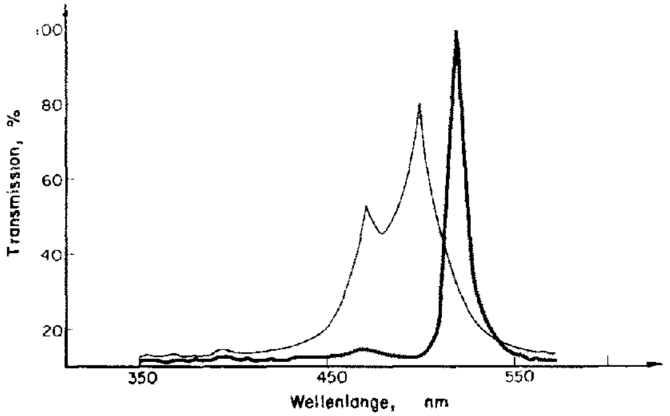

Abb. 1.—Fluoreszenz-Anregungsspektrum von FMA in 0,1n NaOH, Emissionswellenlänge λ_E 520 nm ——
Fluoreszenz-Emissionsspektrum von FMA in 0,1n NaOH, Anregungswellenlänge λ_A 499 nm ——

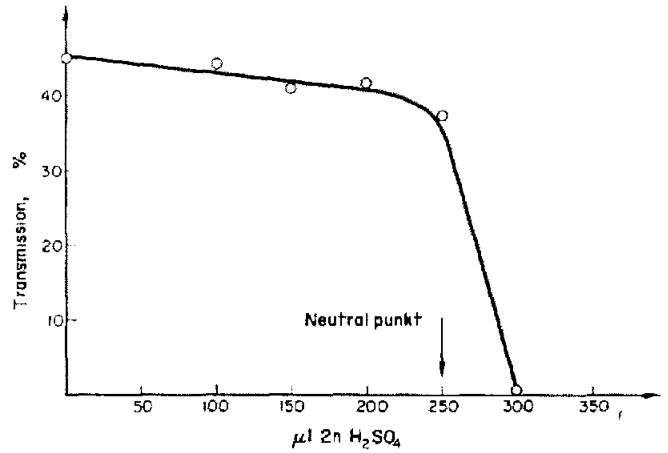

Abb. 2.—Aciditätsabhängigkeit der Fluoreszenzintensität der FMA-Lösung (1n NaOH). Der Intensitätsabfall im alkalischen Bereich wird durch Verdünnung bedingt.

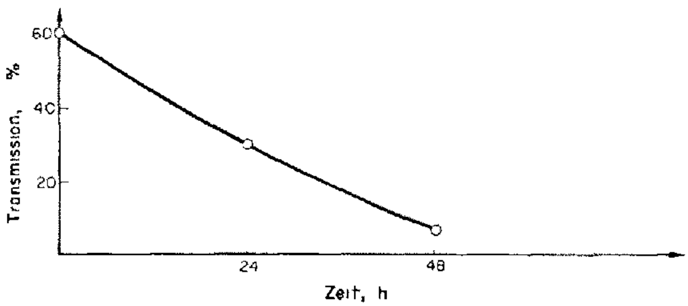

Abb. 3.—Lichtabhängigkeit der Fluoreszenzintensität der 0,1n natronalkalischen FMA-Lösung (8 ng FMA/ml), die im diffusen Tageslicht aufbewahrt wurde.

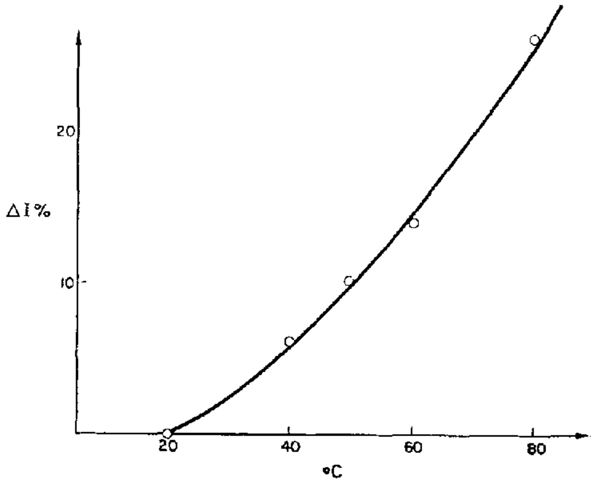

Abb. 4.—Temperaturabhängigkeit der Fluoreszenzintensität der 0,1n natronalkalischen FMA-Lösung (16 ng FMA/ml)
Fluoreszenzintensität bei 20°C = I_0
Fluoreszenzintensität bei >20°C = I_T
$\Delta I = I_0 - I_T$

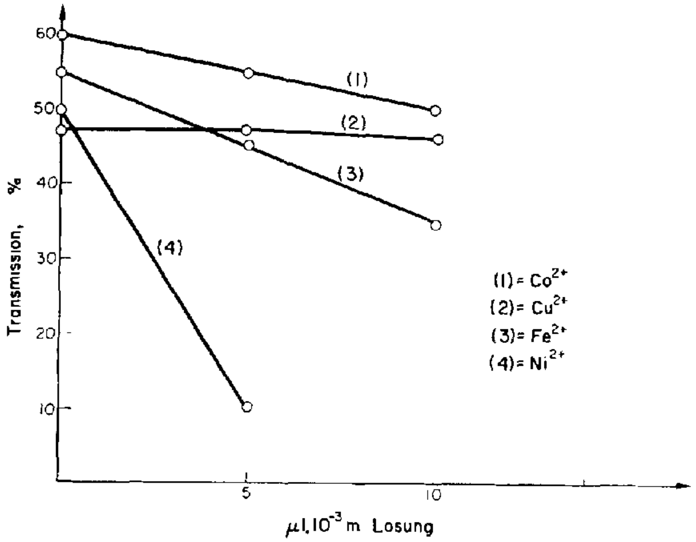

Abb. 5.—Beeinflussung der Fluoreszenzintensität der 0,1n natronalkalischen FMA-Lösung (82,3 ng FMA/ml) durch Kationen.

Wie bei den meisten fluoreszierenden Verbindungen ist auch bei alkalischen FMA-Lösungen eine starke Temperaturabhängigkeit der Fluoreszenzintensität festzustellen. Sie nimmt erwartungsgemäß mit steigender Temperatur ab.

Störungen werden bereits durch die Gegenwart von Fe^{2+}-, Fe^{3+}-, Co^{2+}- und Ni^{2+}-Ionen im Nanogrammbereich verursacht, während Cu^{2+}-, Cd^{2+}-, Alkali- und Erdalkali-Metallionen die Fluoreszenzintensität der FMA-Lösung im Konzentrationsbereich von 0,1–1 µg/ml noch nicht beeinflussen. Fluorid, Chlorid, Bromid

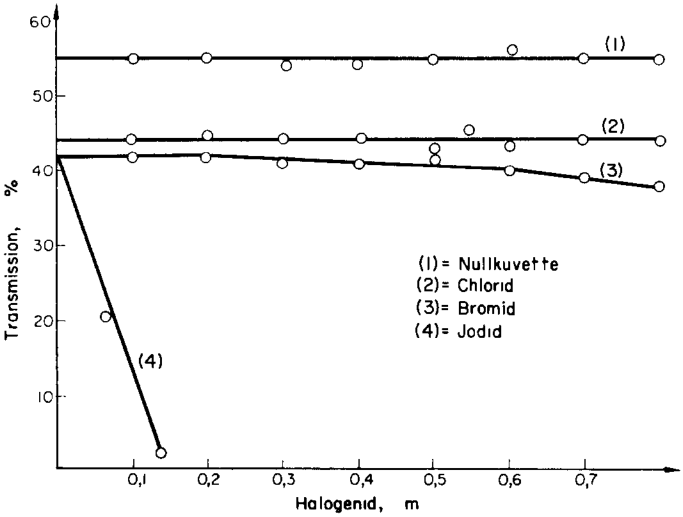

ABB. 6.—Einfluß von Anionen auf die Fluoreszenzintensität; Bedingungen und Konzentration von FMA siehe Diagr. 5.

sowie Nitrat, Sulfat und Phosphat stören ebenfalls nicht, Jodid stört erst in großem Überschuß. Bei einer Jodidkonzentration von 0,07m wird die Fluoreszenzintensität der FMA-Lösung zu 50% gelöscht. Die Fluoreszenz von alkalischen FMA-Lösungen wird durch Sulfidionen proportional der Sulfidkonzentration gelöscht (vgl. Abb. 7).

Mit Hilfe einer zweiten, von der Fluoreszenzlöschung unabhängigen Bestimmungsmethode[2], bei der die Sulfidionen mit einer 0,001n Cadmiumacetatlösung gegen Dithizon titriert wurden, konnte die Stöchiometrie der Reaktion zwischen Sulfid und FMA bestätigt werden. Ein Mol FMA reagiert mit 2 Mol Sulfid. Die Bestimmung von 3,5 ng S^{2-}/ml ließ sich durch die Fluoreszenzlöschreaktion mit einer relativen Standardabweichung von ±4,9% (20 Bestimmungen) reproduzieren.

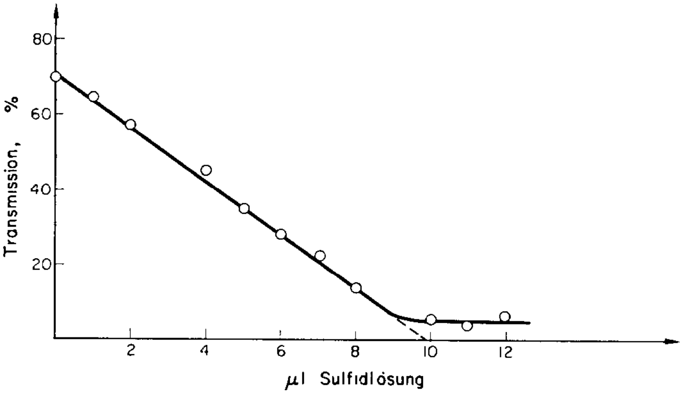

ABB. 7.—Fluoreszenzlöschkurve von 0,1n natronalkalischer FMA-Lösung (82,3 ng FMA/ml) durch Sulfidlösung ($2 \cdot 10^{-5}$m).

Sulfidlösungen sind unter normalen Bedingungen ohne besondere Vorkehrungen umso unbeständiger, je kleiner ihre Sulfidionenkonzentration ist. Da sich im

Schrifttum keine genauen Angaben über die Beständigkeit sehr verdünnter Sulfidlösungen finden, untersuchten wir die Haltbarkeit wäßriger Sulfidlösungen im Bereich von 10^{-7} bis 10^{-5}m mit Hilfe der FMA-Methode. Die Gegenwart von Sauerstoff erwies sich als unwesentlich, wenn die Lösung völlig dunkel aufbewahrt wird. Dagegen ist eine sowohl alkalische als auch neutrale $2 \cdot 10^{-7}$m Sulfidlösung im diffusen Tageslicht sehr unbeständig (Abb. 8). Über das Verhalten "sauerstofffreier" Sulfidlösungen, die nur schwer zu handhaben sind, liegen noch keine Ergbnisse vor. In der Literatur wird als Antioxidans Formaldehyd zur Stabilisierung von Sulfidlösungen vorgeschlagen,[12] was sich aber bei 10^{-7}m Sulfidlösungen als unzureichend erwies

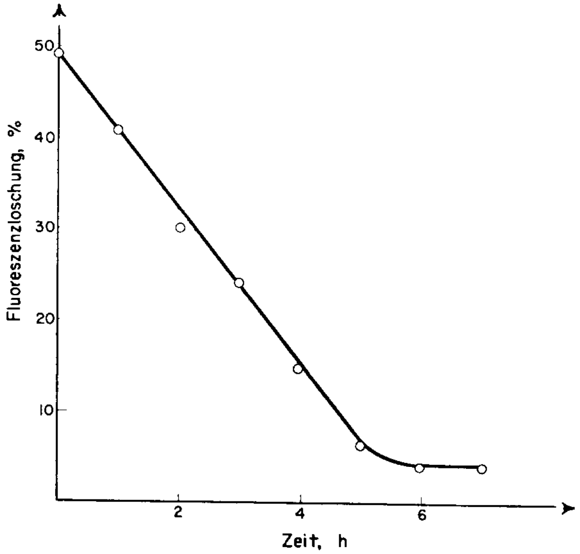

Abb. 8.—Abhängigkeit der Fluoreszenzlöschung vom Alter der Sulfidlösung, die im diffusen Tageslicht aufbewahrt wurde.
Bei jeder Messung (im zeitlichen Abstand von 1 Stunde) wurden 5 μl Sulfidlösung zu jeweils 1 ml FMA-Lösung (82,3 ng FMA/ml) zugegeben. Die Sulfidlösung hatte eine Ausgangskonzentration von $2 \cdot 10^{-5}$m.

Setzt man solche Lösungen dem indirekten Tageslicht aus, so beträgt die Sulfidionenkonzentration nach 8 h weniger als 10% der Ausgangskonzentration.

Sulfidlösungen eignen sich somit schlecht als Standardlösungen. Daher wurde nach Substanzen gesucht, die mit FMA stöchiometrisch reagieren und die Fluoreszenzintensität von FMA-Lösungen proportional zu ihrer Konzentration löschen, aber in verdünnter Lösung beständig sind.

Von den untersuchten Lösungen folgender substituierter Schwefelverbindungen: Diphenylthioäther, Phenylbenzyl-thioäther, Thiophenol, Cystein, Thioharnstoff, Diphenylthioharnstoff, Dithiocarbaminate, Cyanodithioformiate, eignen sich als Standardsubstanzen Thioharnstoff und ganz besonders gut Diphenylthioharnstoff. Lösungen beider Thioharnstoffe verhalten sich über 10 Tage lang sowohl im Dunkeln als auch im diffusen Tageslicht beständig. Als Standardsubstanz wurde Diphenylthioharnstoff vorgezogen, da dieser praktisch augenblicklich mit FMA reagiert, während Thioharnstoff erst nach etwa 30 min maximale Löschung zeigt. Die unterschiedlichen Reaktionszeiten führen zu verschiedenen relativen Standardabweichungen, die sich für 5 μl einer $2 \cdot 10^{-5}$m Thioharnstofflösung pro ml

FMA-Lösung zu 7,5% und bei einer analogen Diphenylthioharnstoffmenge zu 4,8% ergab (Abb. 9). Die anderen Substanzen waren weniger beständig und zeigten zum Teil sehr lange Reaktionszeiten.

Das Bestimmungsverfahren wird durch Kationen gestört, die in alkalischer Lösung schwerlösliche Sulfide bilden. Keine Störungen ergaben sich bei der Bestimmung von 3,5 ng S^{2-}/ml neben dem 1000 fachen Überschuß an F^-, Cl^-, Br^-, SO_4^{2-}, PO_4^{3-}. J^- und NO_3^- zeigen bei einem 50 fachen Überschuß noch keinen störenden Einfluß auf die Bestimmung.

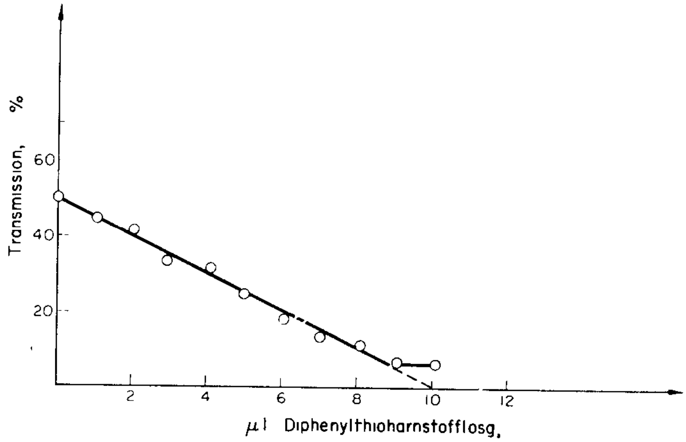

Abb. 9.—Fluoreszenzlöschkurve von 0,1n natronalkalischer FMA-Lösung (82,3 ng FMA/ml) durch Diphenylthioharnstofflösung ($2 \cdot 10^{-5}$m).

Die Methode eignet sich zur Bestimmung sehr kleiner Schwefelmengen besonders in organischen Substanzen nach einem hydrierenden Aufschluß[2], bei dem die störenden Kationen leicht abgetrennt werden können.

EXPERIMENTELLER TEIL

Geräte

*Photofluorometer.**

10 *mm-Quarzküvetten*, allseitig optisch bearbeitet, mit Teflonstopfen verschließbar.

Ultramikrokolbenbürette, mit einer Standardabweichung kleiner als ±0,01 μl. Die Bürettenspitze besteht aus einer möglichst feinen Polyäthylenkapillare, vgl.[8].†

Reagenzien

Fluoreszein-mercuri-acetat-Lösung, 10^{-7}m, *in* 0,1n *Natronlauge* (FMA-Lösung).

Stammlösung. Die FMA-Lösung hat eine Konzentration von 82,3 mg/l. (10^{-4}m). Man stellt sie her, indem man 82,3 mg FMA zu einem Liter 0,1 m-natronalkalischer Lösung auflöst. Die Lösung ist in einem Quarzkolben, gut verschlossen, im Dunkeln mehrere Monate ohne Titerverlust aufzubewahren.

Gebrauchslösung. Die 10^{-7}m Gebrauchslösung wird hergestellt, indem man in einem Quarzmeßkolben 1 ml der Stammlösung zu 1 Liter 0,1 m-natronalkalischer Lösung verdünnt. Diese Lösung ist ebenso wie die Stammlösung in Quarzkolben oder in durch Ausdämpfen künstlich gealterten, braunen Flaschen über mehrere Monate titerkonstant, wenn die Kolben bzw. Flaschen vorher mit der Lösung konditioniert wurden, vgl.[8].

Darstellung des FMA. In einem Rundkolben (1 Liter) mit Rührer, Tropftrichter und Rückflußkühler wurden in 200 ml Eisessig 14 g (0,044 Mol) Quecksilber(II)acetat gelöst. Bei 50°C wurde unter Rühren langsam eine wässrige Lösung von 7,1 g (0,02 Mol) Natriumfluoresceinat zugetropft. Nach dem Zutropfen stellt man die Heizung ab und läßt unter Rühren auf Zimmertemperatur abkühlen. Schon nach kurzer Zeit kann man einen orangegefärbten Niederschlag beobachten, der abfiltriert

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* z. B. "Aminco Bowman" der Firma American Instrument Comp., Inc., Silver Spring, Maryland, USA.

† z. B. System Spinco der Firma Beckman Instruments, München, BRD.

wird. Der Niederschlag wird so lange mit bidestilliertem Wasser gewaschen, bis das abfließende Waschwasser farblos ist. Das Produkt wurde im Vakuum getrocknet. Die Ausbeute betrug 11,5 g, was 68 % der Theorie entspricht.

Sulfidstandardlösung

Diphenylthioharnstoff-Lösung, $2 \cdot 10^{-5}$m.

Stammlösung. Die $2 \cdot 10^{-3}$m Stammlösung stellt man her, indem man 45,6 mg Diphenylthioharnstoff in 20 ml reinstem Methanol löst und in einem 100-ml Quarzmeßkolben bis zur Marke mit bidestilliertem Wasser auffüllt. Gut verschlossen aufbewahrt, zeigt diese Lösung über mehrere Wochen keine Konzentrationsänderung.

Gebrauchslösung. Die $2 \cdot 10^{-5}$m Gebrauchslösung wird hergestellt, indem man in einem 1000-ml Quarzmeßkolben 10 ml der Stammlösung mit bidestilliertem Wasser zu 1000 ml Lösung verdünnt. Diese Lösung blieb ohne besondere Schutzmaßnahmen über 10 Tage titerkonstant.

Anerkennung—Zur Bereitung wäfrigen Lösungen ist bidestelliertes Wasser (Destillations apparatur aus Quarz) zu verwenden.

Durchführung der Bestimmung

Aufstellung der Eichkurve. In vier sorgfältig gereinigten Küvetten* werden jeweils genau 1,00 ml FMA-Lösung mit Hilfe einer Kolbenbürette vorgelegt. Die Küvetten werden mit Teflonstopfen verschlossen. Dann dosiert man in 3 Küvetten gleiche Mengen der Diphenylthioharnstofflösung im Bereich von 1 bis 10 μl aus der Ultramikrokolbenbürette. Die Küvetten werden wieder verschlossen und 5 mal geschüttelt. Man mißt die Fluoreszenzintensität und wiederholt die Messung im Abstand von 5 Minuten. Die Verweilzeit der Küvetten im Meßgerät muß möglichst kurz und konstant sein. In der Zeit zwischen den Messungen müssen die Küvetten im Dunkeln aufbewahrt werden. Aus den sich so ergebenden 6 Meßwerten wird der Mittelwert gebildet. Eventuelle Veränderungen der Fluoreszenzintensität der FMA-Lösung bestimmt man mit der vierten Küvette (Nullwertküvette), deren Intensität vor und nach der Meßserie gemessen wird. Man stellt eine Eichkurve auf, indem man die prozentuale Fluoreszenzschwächung bzw. die Fluoreszenzintensität selbst gegen die vorgelegte Schwefelmenge aufträgt.

Zur Bestimmung von Schwefel nach einem hydrierenden Aufschluß[2] überführt man den gebildeten Schwefelwasserstoff mit Hilfe eines "sauerstofffreien" Trägergases unmittelbar in die Küvette, in der er in der vorgelegten FMA-Lösung absorbiert wird. Über Einzelheiten der Durchführung des Aufschlusses wird demnächst berichtet. Die Bestimmung erfolgt analog der Vorschrift zur Aufstellung der Eichkurve.

Résumé—On décrit le dosage du sulfure dans le domaine 1–10 ng/ml basé sur l'extinction de fluorescence de la fluorescéine–acétate mercurique en solution alcaline. On a utilisé des solutions de diphénylthiourée comme standards d'étalonnage. L'écart type est de 0,17 ng/ml pour 3,5 ng de sulfure par ml.

Summary—The determination of sulphide in the range 1–10 ng/ml based on the quenching of the fluorescence of fluorescein-mercuric acetate in alkaline solution is described. Solutions of diphenylthiourea were used as calibration standards. The standard deviation was 0·17 ng/ml for 3·5 ng/ml of sulphide.

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* Die Küvetten werden mit Königswasser gereinigt. Anschließend mit bidestilliertem Wasser und reinstem Methanol gespült. Die Entfernung des Methanols erfolgt im Vakuumexsikkator.[11]

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STUDIES ON IMIDAZOLE DERIVATIVES AS CHELATING AGENTS—V*

INVESTIGATIONS OF THE APPLICABILITIES OF THE AZOIMIDAZOLES AS METALLOCHROMIC INDICATORS

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Summary—Applicabilities of several azoimidazoles as metallochromic indicators were investigated in the light of the general equations expressing the colour change of the visual chelatometric titrations. By using the stability constants of the nickel(II), copper(II), zinc(II) and cadmium(II) chelates, the useful pH ranges, titration errors and sharpness of colour changes were predicted theoretically and the usefulness of these reagents as indicators was established experimentally. The Cu(II)-EDTA-indicator system was also examined experimentally. The OH-containing azoimidazoles could be applied to the direct titration of copper, nickel, zinc, cadmium, lead and bismuth and to the titration of calcium and cobalt in the presence of Cu(II)-EDTA. Attempts were made to construct diagrams for the estimation of titration errors and sharpness of colour changes.

FROM the practical point of view, visual end-point detection is of great importance in chelatometry. The stabilities of the metal chelates of the azoimidazoles reported in a previous paper[1] suggested that these imidazoles can be successfully applied as metallochromic indicators in chelatometric titrations. In the present paper, the analytical applicabilities of the azoimidazoles were first estimated by means of the theoretical equations expressing the colour change near the end-point, because the titration conditions may have a decisive effect on the analytical results, and then their usefulness as indicators was experimentally established and compared with that of 1-(2-pyridylazo)-2-naphthol(PAN) and Eriochrome Black T. The applicabilities of the copper(II)-EDTA-indicator system were also examined experimentally.

Construction of diagrams was attempted with a view to facilitating the estimation of the titration error and the sharpness of the colour change at the end-point. They would serve as a means of predicting the accuracy and the facility with which visual titration with an indicator forming a 1:1 metal complex could be carried out.

Derivation of equations‡

Theoretical treatment of the colour change near the end-point of the titration has been reported by several authors. Fortuin *et al.*[2] and Flaschka and Khalafallah[3] derived the fundamental equations expressing the colour change during a titration involving an indicator L which reacts with a metal M to form a complex ML. Reilley

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‡ The charges of the ions are omitted for simplicity.

and Schmid[4] later refined the equations by introducing "end-point indices" and made them more suitable for practical use. As the azoimidazoles usually form chelates with metal:ligand ratios other than 1:1, it was necessary to use the equations applicable to the indicators which are capable of forming metal complexes, ML_N. Kotrlý[5] and Tanaka and Nakagawa[6] reported the general equations which take the stepwise formation of metal–indicator complexes into consideration, but they made some simplifications in deriving them. As the amount of indicator is not always negligible and it would sometimes be necessary to consider all the stepwise equilibria, another general expression of the ratio of titrant to metal was derived by extending the relationships described by Fortuin *et al.* and Flaschka and Khalafallah. The presence of a second metal ion was not considered in deriving the equations.

The fundamental equations expressing the stoichiometric relationships in the solution being titrated may be written as follows

$$C_M = [M] + [MY] + [ML] + [ML_2] + \cdots + [ML_N] \tag{1}$$

$$C_Y = [Y] + [MY] \tag{2}$$

$$C_L = [L] + [ML] + 2[ML_2] + \cdots + N[ML_N] \tag{3}$$

where C_M, C_Y and C_L are the total concentrations of metal, titrant and indicator respectively, and [M], [Y] and [L] are the concentrations of free metal ion, free titrant and free indicator respectively. [MY], [ML], $[ML_2]$, *etc.* are the concentrations of the metal–titrant and metal–indicator complexes respectively, with stability constants given by

$$K_{MY} = \frac{[MY]}{[M][Y]} \tag{4}$$

$$K_{ML} = \frac{[ML]}{[M][L]}\,;\quad K_{ML_2} = \frac{[ML_2]}{[ML][L]}\,;\quad \cdots \tag{5}$$

Combination of equations (1) to (5) gives

$$C_L = [L] + K_{ML}[M][L] + 2K_{ML}K_{ML_2}[M][L]^2 + \cdots + NK_{ML}\cdots K_{ML_N}[M][L]^N. \tag{6}$$

The ratio of titrant to metal, x, and that of free ligand to total ligand, y, are expressed as

$$x = C_Y/C_M \tag{7}$$

$$y = [L]/C_L. \tag{8}$$

It was assumed here that all the metal–indicator complexes contribute equally to the colour development.

From equations (6) and (8), the equation for [M] at a given value of y is obtained

$$[M] = \frac{1 - y}{\sum_{n=1}^{N} n y^n C_L^{n-1} \beta_n} \tag{9}$$

where $\beta_n = K_{ML}K_{ML_2}\cdots K_{ML_n}$. Combination of equations (1), (2), (4), (5), (7) and (8) gives the expression for x at a given value of y

$$x = 1 + \frac{1}{K_{MY}[M]} - \frac{[M]}{C_M} - \frac{1}{C_M K_{MY}}\left\{1 + (1 + K_{MY}[M])\sum_{n=1}^{N} y^n C_L{}^n \beta_n\right\}. \quad (10)$$

The function $x = f(y)$ can be obtained by combining equations (9) and (10).

As the auxiliary complexing agents and protons in the solution lead to side-reactions and affect the stabilities of the complexes MY, ML, ML_2, *etc.*, equations (9) and (10) should be rewritten as (11) and (12), respectively, by introducing the side-reaction coefficients α_{HY}, α_{HL}, α_{MY} and γ.

$$[M]' = \frac{(1-y)\gamma}{\sum_{n=1}^{N} n y^n C_L^{n-1}\beta_n/\alpha_{HL}{}^n} \quad (11)$$

$$x = 1 + \frac{\alpha_{HY}\gamma}{\alpha_{MY}K_{MY}[M]'} - \frac{[M]'}{C_M} - \frac{1}{\alpha_{MY}C_M K_{MY}}$$
$$\times\left\{\alpha_{HY}\gamma + (\alpha_{HY} + \alpha_{MY}K_{MY}[M]'/\gamma)\sum_{n=1}^{N} y^n C_L{}^n \beta_n/\alpha_{HL}{}^n\right\} \quad (12)$$

The side-reaction coefficients can be calculated by the following equations from the pH of the solution, the acid dissociation constants of the titrant, k_1–k_t, and indicator, k_1'–k_i', the stability constants of the hydrogen complex, K_{MHY}, and the hydroxo complex, $K_{M(OH)Y}$, and the stability constants of the metal complexes of auxiliary complexing agents, K_{A1}–K_{Am}.

$$\alpha_{HY} = 1 + \frac{[H]}{k_t} + \frac{[H]^2}{k_t k_{t-1}} + \cdots + \frac{[H]^t}{k_t k_{t-1}\cdots k_1}$$

$$\alpha_{HL} = 1 + \frac{[H]}{k_i'} + \frac{[H]^2}{k_i' k_{i-1}'} + \cdots + \frac{[H]^i}{k_i' k_{i-1}'\cdots k_1'}$$

$$\alpha_{MY} = 1 + [H]K_{MHY} + [OH]K_{M(OH)Y}$$

$$\gamma = 1 + [A]K_{A1} + [A]^2 K_{A1}K_{A2} + \cdots + [A]^m K_{A1}\cdots K_{Am}$$

where [A] is the concentration of free auxiliary complexing agent.

The sharpness of the colour change at the end-point may be predicted from the dy/dx values.[2,4,6] For the case where $n = 2$, dy/dx is derived from equations (11) and (12) as

$$\frac{dy}{dx} = 1\Big/\left\{\frac{\partial x}{\partial y} + \frac{\partial x}{\partial [M]'}\frac{d[M]'}{dy}\right\} \quad (13)$$

The terms $\partial x/\partial y$, $\partial x/\partial[M]'$ and $d[M]'/dy$ are given by the following equations

$$\frac{\partial x}{\partial y} = -\frac{C_L K_{ML}'(1 + K_{MY}'[M]')(1 + 2yC_L K_{ML_2})}{C_M K_{MY}'} \quad (14)$$

$$\frac{\partial x}{\partial [M]'} = -\frac{1}{K_{MY}'[M]'^2} - \frac{1}{C_M}\{1 + yC_L K_{ML}'(1 + yC_L K_{ML_2}')\} \quad (15)$$

$$\frac{d[M]'}{dy} = -\frac{1 + 2yC_L K_{ML_2}'(2 - y)}{y^2 K_{ML}'(1 + 2yC_L K_{ML_2}')^2} \quad (16)$$

where K_{MY}', K_{ML}' and K'_{ML_2} are the conditional constants defined as:

$$K_{MY}' = \alpha_{MY}K_{MY}/\alpha_{HY}\gamma; \; K_{ML}' = K_{ML}/\alpha_{HL}\gamma; \; K'_{ML_2} = K_{ML_2}/\alpha_{HL}.$$

If the stability constants, the acid dissociation constants and the pH of the solution are known, the course of the colour change during the titration can be estimated for a given set of C_M and C_L by plotting y against x.

EXPERIMENTAL

Calculations

In order to achieve precise and rapid calculations of a number of values, the KDC-II(Hitachi HITAC 5020) digital computer of Kyoto University Computation Center was used. The flow diagram of the programme written in HARP 5020 (FORTRAN IV) is shown in Fig. 1. The side-reaction coefficient, γ, was calculated by assuming the presence of 0·1M acetate (pH <8) and 0·1M ammonia (pH ≥8). The x values were calculated from equations (11) and (12) and compared with the values calculated according to Reilley and Schmid[4] and Tanaka and Nakagawa.[6] The stability constants of the metal complexes which appeared in the calculations were obtained from the preceding paper[1] and the monograph of Ringbom.[7]

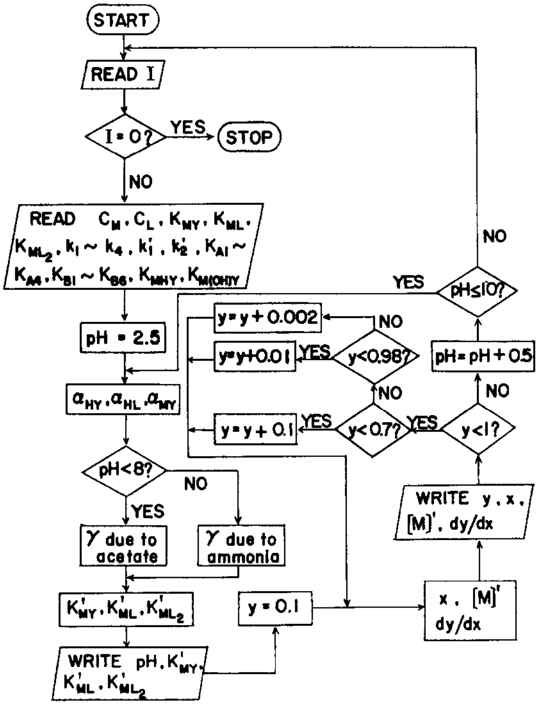

FIG. 1.—Flow diagram for computer programme.

Reagents

Indicators. The following four azoimidazoles[8] were used as 0·1% solutions in ethanol: 1-[4-methyl-5-imidazolylazo]-2-naphthol(IAN); 2-[4-methyl-5-imidazolylazo]-4-methoxyphenol(IAM); 3-dimethylamino-6-[4-methyl-5-imidazolylazo]phenol(DIP); (4-methyl-5-imidazolylazo)-4-dimethylaminobenzene(DAI).

Standard metal ion solutions, 0·01M. Prepared and standardized as described in the preceding paper.[1]

EDTA solution, 0·01M. Standardized against standard zinc with Eriochrome Black T as indicator.

Copper(II)*-EDTA solution*, 0·005*M*. Prepared by mixing equal volumes of 0·01*M* copper(II) nitrate and 0·01*M* EDTA.

All the reagents used were of reagent grade. Demineralized water was used throughout.

Apparatus

Shimadzu photometric titration apparatus attached to a Shimadzu Model QR-50 spectrophotometer. Radiometer Titrator TTT1.

Procedures

Direct titrations. To 2–5 ml of a metal ion solution were added 15 ml of a buffer solution (0·1*M*) and 2 drops of an indicator, and the resulting solution was titrated with 0·01*M* EDTA until the colour of the solution became yellow. If the metal–indicator complex precipitated, 10 ml of ethanol were added and the solution was warmed. Precipitation of metal hydroxides was avoided by adding 1 ml of 1*M* potassium sodium tartrate.

Titrations in the presence of copper(II)*-EDTA.* To 2–5 ml of a metal ion solution were added 15 ml of a buffer solution, 5 drops of 0·005*M* copper(II)-EDTA and 2 drops of an indicator. Ethanol and 1*M* potassium sodium tartrate were added when necessary. The solution was titrated with 0·01*M* EDTA. The colour change at the end point was from red to yellow.

Photometric titrations. Photometric titrations were carried out in 50% v/v dioxan–water in order to keep the same conditions as were employed in the determination of the stability constants of the metal–indicator chelates. Five ml of a metal ion solution, 12·5 ml of a buffer solution, 20 ml of dioxan and 0·5 ml of $10^{-3}M$ solution of IAN in ethanol were mixed in a titration vessel and titrated with 0·01*M* EDTA. The absorbance was measured at the wavelength of maximum absorption of the metal–IAN chelate.

RESULTS AND DISCUSSION

By using equations (11) and (12), $-\log\,[\mathrm{M}]'$ and x were calculated by varying y from 0·1 to 1·0 at various pH values on the assumption that 0·1*M* acetate and 0·1*M* ammonia were present as buffers in the acid and the alkaline region, respectively, and acting as auxiliary complexing agents. When $C_{\mathrm{M}}/C_{\mathrm{L}}$ was sufficiently large, x values calculated by equations (11) and (12) coincided approximately with those calculated according to Tanaka and Nakagawa.[6] When K_{ML}' was sufficiently large, x values could also be calculated by neglecting the constants for the higher complexes, *e.g.*, K'_{ML_2} and K'_{ML_3}.

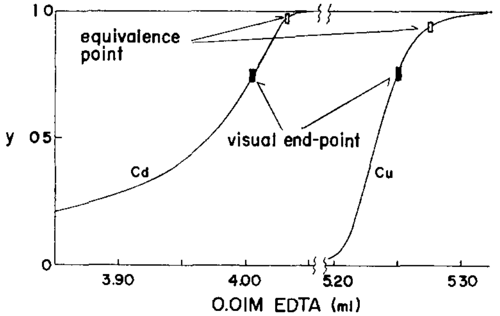

FIG. 2.—Photometric titration curves for copper(II) and cadmium(II) in 50% v/v dioxan-water with IAN as an indicator.

Copper(II)—pH = 6·0; $\lambda = 532$ mμ
Cadmium(II)—pH = 9·8; $\lambda = 510$ mμ

In order to determine the value of y at the visual end-point, the absorbance of a solution being titrated was measured when the visual end-point was attained and the degree of colour change at this point was estimated by comparison with a photometric titration carried out under the same conditions. The photometric titration curves of copper(II) and cadmium(II) with IAN as an indicator are shown in Fig. 2. Usually the visual end-point was found to correspond to $y = 0{\cdot}75$–$0{\cdot}85$, and as far as the azoimidazole IAN was concerned, it was difficult to distinguish the colour at $y = 0{\cdot}75$ from that at $y = 0{\cdot}85$. It may be assumed therefore that in the visual titrations the colour change seems to be complete to the eye when $y = 0{\cdot}8$ and that, as has been reported by several authors,[2,4,6] dy/dx at $y = 0{\cdot}8$ gives a measure of the sharpness of the colour change.

The predicted colour changes during the titrations of nickel(II), copper(II), zinc(II) and cadmium(II) with IAN as indicator and EDTA as titrant are illustrated in Fig. 3. It is possible to predict the sharpness of the colour change and the optimum pH ranges from the curves. The titration errors and the sharpness of the colour change at $y = 0{\cdot}8$ predicted for the azoimidazoles, Eriochrome Black T (EBT) and PAN are summarized in Table I. The sharpness was calculated according to equation (13). Examples of the plots of the sharpness against pH and y are shown in Figs. 4 and 5, respectively.

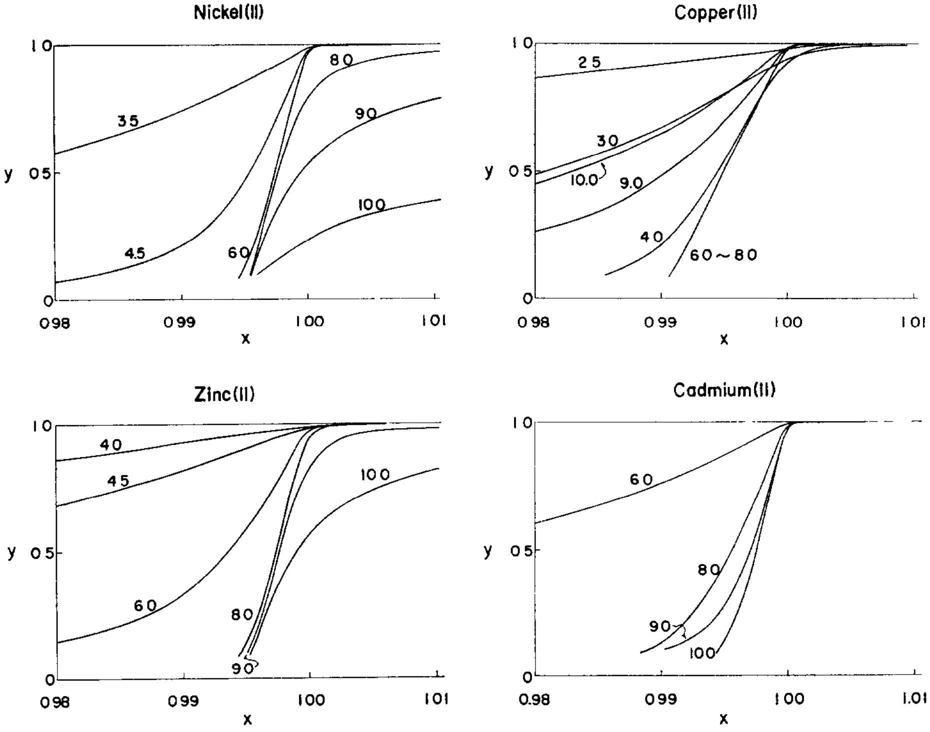

FIG. 3.—Colour change curves.
Indicator: IAN; $C_M = 0{\cdot}0025M$; $C_L = 0{\cdot}000025M$. The numbers on the curves show the pH values of the solution.

It is expected from the calculations that the *o*-hydroxyphenylazoimidazoles IAN, IAM and DIP make it possible to determine nickel(II), copper(II), zinc(II) and cadmium(II) in the pH ranges 3·5–10, 3–10, 4·5–10 and 4·5–10, respectively, to within ±1%, and that the phenylazoimidazole DAI can be applied to the titration of copper(II) in the pH range 3·5–8·0. On the other hand, the pH ranges predicted for

EBT, 9–10 for magnesium(II) and 6–10 for zinc(II), correspond well with the pH ranges already established experimentally. The colour change of zinc(II)–EBT is estimated to be very sharp, since log dy/dx ~ 1·9 at pH 10 (log $K_{MY}' = 11{\cdot}6$; log $K_{ML}' = 6{\cdot}8$; log $K'_{ML_2} = 5{\cdot}5$). The use of PAN for copper(II) in the acid region is believed to give rise to serious positive errors and, as pointed out by Wada and Nakagawa,[9] this may be one of the explanations for the slow colour change observed experimentally. These errors are due to the high stability of the copper(II)–PAN chelate (log K_{ML} ~ 16)[10] but they will be smaller if 1,2-cyclohexanediaminetetraacetic acid (log $K_{MY} = 21{\cdot}3$) is used in place of EDTA.

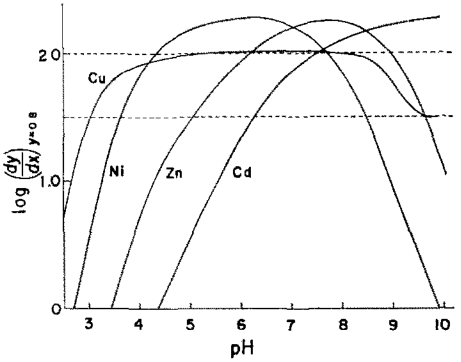

FIG. 4.—Plot of sharpness against pH.
Indicator: IAN; $C_M = 0{\cdot}0025M$; $C_L = 0{\cdot}000025M$.

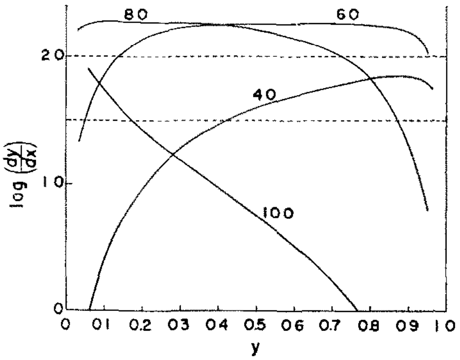

FIG. 5.—Plot of sharpness against y.
Indicator: IAN; metal: nickel(II); $C_M = 0{\cdot}0025M$; $C_L = 0{\cdot}000025M$. The numbers on the curves show the pH values of the solution.

If the change of the absorbance is followed with an instrument as in the case of the photometric titration, it will be possible to detect the end-point correctly from these calculations.

Applications to chelatometry

Direct titrations. The compounds IAN, IAM and DIP were applied to the direct titrations of nickel(II), copper(II), zinc(II), cadmium(II), lead(II) and bismuth(III). The results, along with the comments on the colour change, are summarized in

TABLE I.—PREDICTION OF TITRATION ERRORS AND SHARPNESS OF COLOUR CHANGES AT $y = 0{\cdot}8$ FOR VISUAL EDTA TITRATIONS

Indicator	Metal ion	C_M ($\times 10^{-3}M$)	C_L ($\times 10^{-5}M$)	Error(%)										
				pH										
				2·5	3·0	3·5	4·0	4·5	6·0	8·0	8·5	9·0	9·5	10·0
IAN	Ni(II)	2·5	2·5	−37·5	−4·33	−0·72	−0·26	−0·16	−0·10	+0·02	+0·29	+1·17	+4·32	+17·9
	Cu(II)	0·5	2·5	−16·0	−2·72	−1·23	−1·05	−1·02	−1·00	−1·01	−1·07	−1·54	−2·55	−2·48
	Cu(II)	2·5	2·5	−3·16	−0·51	−0·22	−0·19	−0·20	−0·20	−0·20	−0·21	−0·31	−0·51	−0·49
	Cu(II)	10·0	5·0	−0·81	−0·15	−0·08	−0·08	−0·09	−0·10	−0·10	−0·01	−0·13	−0·18	−0·17
	Zn(II)	2·5	2·5	—	−96·0	−13·6	−2·97	−1·11	−0·21	−0·10	−0·08	−0·03	+0·14	+0·85
	Cd(II)	2·5	2·5	—	—	—	−41·4	−12·3	−0·80	−0·16	−0·13	−0·11	−0·10	−0·10
IAM	Ni(II)	2·5	2·5	—	−14·8	−2·03	−0·50	−0·26	−0·12	−0·10	−0·09	−0·06	+0·02	+0·35
	Cu(II)	2·5	2·5	−4·33	−0·65	−0·24	−0·20	−0·20	−0·20	−0·20	−0·21	−0·31	−0·53	−0·53
	Zn(II)	2·5	2·5	—	—	—	−26·8	−8·41	−0·65	−0·18	−0·16	−0·15	−0·14	−0·11
	Cd(II)	2·5	2·5	—	—	—	—	—	−11·84	−0·32	−0·31	−0·29	−0·21	−0·13
DIP	Ni(II)	2·5	2·5	−65·2	−6·79	−0·88	−0·27	−0·19	−0·09	+0·37	+1·39	+4·75	+16·8	+69·1
	Cu(II)	2·5	2·5	−17·7	−2·06	−0·42	−0·23	−0·20	−0·20	−0·20	−0·21	−0·25	−0·34	−0·33
	Zn(II)	2·5	2·5	—	—	—	−15·4	−2·83	−0·22	−0·10	−0·08	−0·05	+0·09	+0·63
	Cd(II)	2·5	2·5	—	—	−28·3	−3·54	−0·71	−0·19	−0·10	−0·07	+0·01	+0·29	+1·49
DAI	Cu(II)	0·5	2·5	—	−38·5	−7·59	−1·91	−0·89	−0·57	−16·7	—	—	—	—
	Cu(II)	2·5	2·5	−35·1	−7·70	−1·52	−0·38	−0·18	−0·11	−3·34	−99·7	—	—	—
	Cu(II)	2·5	5·0	−29·0	−5·39	−1·03	−0·35	−0·24	−0·21	−1·83	−50·2	—	—	—
EBT	Mg(II)	2·5	2·5	—	—	—	—	—	—	−3·87	−1·08	−0·21	+0·11	+0·32
	Zn(II)	2·5	2·5	—	—	—	−13·5	−2·09	−0·20	−0·18	−0·16	−0·13	−0·09	−0·01
PAN	Cu(II)	2·5	2·5	+18·6	+7·17	+2·64	+0·80	+0·13	−0·18	−0·19	−0·19	−0·20	−0·20	−0·20
	Cu(II)*	2·5	2·5	+10·2	+1·87	+0·22	−0·11	−0·17	−0·20	−0·20	−0·20	−0·20	−0·21	−0·21
	Zn(II)	2·5	2·5	—	—	−36·0	−13·4	−5·97	−0·38	−0·10	−0·09	−0·08	−0·03	+0·18

* Titrant: 1,2-cyclohexanediaminetetra-acetic acid.

Indi-cator	Metal ion	C_M ($\times 10^{-3}M$)	C_L ($\times 10^{-5}M$)	Sharpness (log dy/dx)										
				pH										
				2·5	3·0	3·5	4·0	4·5	6·0	8·0	8·5	9·0	9·5	10·0
IAN	Ni(II)	2·5	2·5	—	0·570	1·361	1·834	2·057	2·270	1·847	1·466	1·000	0·473	—
	Cu(II)	0·5	2·5	0·004	0·789	1·161	1·255	1·280	1·299	1·301	1·263	1·075	0·834	0·847
	Cu(II)	2·5	2·5	0·698	1·463	1·809	1·913	1·959	1·997	1·999	1·961	1·774	1·532	1·545
	Cu(II)	10·0	5·0	1·264	1·888	2·097	2·183	2·244	2·297	2·300	2·280	2·173	2·007	2·016
	Zn(II)	2·5	2·5	—	—	0·071	0·732	1·169	1·939	2·248	2·180	1·997	1·646	1·116
	Cd(II)	2·5	2·5	—	—	—	—	0·115	1·325	2·088	2·172	2·240	2·275	2·284
IAM	Ni(II)	2·5	2·5	—	0·035	0·904	1·537	1·848	2·188	2·277	2·233	2·112	1·849	1·413
	Cu(II)	2·5	2·5	0·565	1·381	1·796	1·915	1·960	1·997	1·999	1·960	1·765	1·514	1·512
	Zn(II)	2·5	2·5	—	—	—	—	0·281	1·421	2·033	2·072	2·062	2·092	2·209
	Cd(II)	2·5	2·5	—	—	—	—	—	0·132	1·786	1·745	1·742	1·885	2·127
DIP	Ni(II)	2·5	2·5	—	0·375	1·275	1·827	1·991	2·217	1·395	0·933	0·433	—	—
	Cu(II)	2·5	2·5	—	0·896	1·610	1·895	1·960	1·996	1·998	1·981	1·884	1·731	1·740
	Zn(II)	2·5	2·5	—	—	—	0·019	0·758	1·918	2·251	2·204	2·053	1·737	1·226
	Cd(II)	2·5	2·5	—	—	—	0·657	1·367	1·990	2·201	2·110	1·871	1·466	0·907
DAI	Cu(II)	0·5	2·5	—	—	0·274	0·892	1·268	1·515	1·525	—	—	—	—
	Cu(II)	2·5	2·5	—	0·280	0·972	1·589	1·965	2·213	2·224	—	—	—	—
	Cu(II)	2·5	5·0	—	0·425	1·152	1·668	1·879	1·975	1·978	—	—	—	—
EBT	Mg(II)	2·5	2·5	—	—	—	—	—	—	0·435	0·947	1·225	1·346	1·321
	Zn(II)	2·5	2·5	—	—	—	0·075	0·891	1·974	2·004	2·033	2·081	2·089	1·909
PAN	Cu(II)	2·5	2·5	—	0·327	0·726	1·139	1·511	1·954	1·980	1·979	1·970	1·951	1·947
	Cu(II)*	2·5	2·5	0·152	0·855	1·439	1·786	1·928	1·996	1·998	1·997	1·988	1·971	1·972
	Zn(II)	2·5	2·5	—	—	—	0·077	0·429	1·633	2·282	2·262	2·189	1·995	1·584

* Titrant: 1,2-cyclohexanediaminetra-acetic acid.

TABLE II.—APPLICATIONS TO DIRECT EDTA TITRATIONS

Indicator	Metal ion	Medium	pH	Taken, *mg*	Found, *mg*	Comments on colour change
IAN	Ni(II)	H_2O	3·5	1·25	1·25	clear and sharp
		H_2O	5·1	1·25	1·25	clear and sharp
		EtOH–H_2O*	5·6	1·25	1·25	clear and sharp
		EtOH–H_2O*	8·8	1·25	1·27	clear and sharp
		EtOH–H_2O*	9·7	1·25		no colour change
	Cu(II)	H_2O	2·5	0·64	0·64	not clear
		H_2O	4·3	0·64	0·63	clear and sharp
		EtOH–H_2O	4·5	1·96	1·97	clear and sharp
		EtOH–H_2O	7·6	1·31	1·31	clear
		EtOH–H_2O	10·0	1·31	1·33	clear
	Zn(II)	H_2O	6·9	1·40	1·40	not clear
		EtOH–H_2O	8·0	1·33	1·32	not clear
		EtOH–H_2O	9·0	1·40	1·42	clear and sharp
		EtOH–H_2O	10·0	1·33	1·34	clear and sharp
	Cd(II)	EtOH–H_2O	10·0	3·35	3·35	not clear
	Pb(II)	H_2O	6·0	6·08	6·07	not clear
		H_2O	7·0	6·08	6·04	not clear
		H_2O	7·5	6·08	6·08	clear
		H_2O	8·5	6·08	6·08	clear and sharp
		H_2O	10·1	6·08	6·09	clear
		H_2O	10·5	6·08	6·10	not clear
	Bi(III)	H_2O	1·0	5·79	5·80	clear and sharp
		H_2O	1·2	1·93	1·92	clear and sharp
		H_2O	2·1	5·79	5·80	clear and sharp
		H_2O	3·5	5·79	5·82	clear and sharp
		H_2O	3·6	5·79	5·81	clear
		H_2O	4·1	5·79	5·81	clear
IAM	Ni(II)	H_2O	3·0	1·25	1·10	not clear
		H_2O	3·6	1·25	1·24	not clear

		H_2O	4·5	1·25	1·26	not clear
		EtOH–H_2O	6·9	1·25	1·27	clear
		EtOH–H_2O	10·0	1·25	1·26	clear
	Cu(II)	H_2O	2·5	1·32	1·32	clear and sharp
		H_2O	4·5	1·32	1·32	clear and sharp
		EtOH–H_2O	10·0	1·32	1·33	clear
	Zn(II)	H_2O	6·9	1·40	1·38	not clear
		H_2O	9·0	1·40	1·42	clear and sharp
		EtOH–H_2O	10·0	1·40	1·39	clear and sharp
	Cd(II)	EtOH–H_2O	10·0	3·35	3·35	clear
	Pb(II)	H_2O	5·7	6·25	5·81	not clear
		H_2O	10·0	4·16	4·15	clear
	Bi(III)	H_2O	1·0	5·79	5·40	not clear
		H_2O	1·4	5·79	5·79	clear and sharp
		H_2O	4·0	5·79	5·77	not clear
DIP	Ni(II)	H_2O	4·5	1·25	1·26	not clear
		EtOH–H_2O	10·0	1·25	1·29	not clear
	Cu(II)	H_2O	2·6	2·64	2·65	not clear
		EtOH–H_2O	4·5	1·32	1·33	clear
		EtOH–H_2O	5·7	2·64	2·65	clear
		EtOH–H_2O	10·0	2·64	2·65	clear
	Zn(II)	EtOH–H_2O	6·9	1·40	1·41	clear
		EtOH–H_2O	9·0	1·40	1·40	clear and sharp
		EtOH–H_2O	10·1	2·61	2·60	clear
	Cd(II)	EtOH–H_2O	10·0	3·35	3·34	clear
	Pb(II)	H_2O	5·7	6·25	5·97	not clear
		H_2O	10·0	4·16	4·15	clear and sharp
DAI	Cu(II)	H_2O	2·8	0·65	0·65	not clear
		H_2O	3·0	0·65	0·65	clear
		H_2O	4·5	1·31	1·33	clear and sharp
		EtOH–H_2O	6·7	0·65	0·64	clear and sharp

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* Aqueous ethanol.

Table II. In most cases a colour change from red or reddish violet to yellow was observed. Addition of ethanol and heating were often necessary in order to obtain sharp colour changes in neutral and alkaline solutions. Copper(II) and nickel(II) were successfully titrated in the pH range 3–10, whereas zinc(II), cadmium(II) and lead(II) could be titrated easily in alkaline solution. Titration of bismuth(III) was possible in strongly acid solution.

TABLE III.—APPLICATIONS TO Cu(II)–EDTA–INDICATOR SYSTEMS

Indicator	Metal ion	Medium	pH	Taken, *mg*	Found, *mg*	Comments on colour change
IAN	Co(II)	EtOH–H_2O*	3·7	1·17	1·18	clear
		EtOH–H_2O*	6·2	1·17	1·17	clear
		EtOH–H_2O*	10·0	1·17	1·16	not clear
	Ni(II)	H_2O	3·1	1·25	1·26	clear
		EtOH–H_2O	5·6	2·50	2·50	clear
		EtOH–H_2O	8·8	1·25	1·26	clear
		EtOH–H_2O	9·8	1·25	1·26	clear
	Cd(II)	H_2O	5·6	3·35	3·35	clear
		EtOH–H_2O	10·0	3·35	3·35	clear
	Ca(II)	H_2O	8·0	0·81	0·81	clear
		H_2O	8·5	0·81	0·82	clear
		H_2O	10·1	0·81	0·80	clear
IAM	Co(II)	EtOH–H_2O	3·7	0·59	0·58	clear
	Ni(II)	EtOH–H_2O	3·7	0·62	0·61	clear
	Cd(II)	EtOH–H_2O	4·5	3·35	3·29	not clear
		EtOH–H_2O	5·6	3·35	3·35	clear
		EtOH–H_2O	10·0	3·35	3·33	clear
	Ca(II)	H_2O	10·0	0·41	0·42	clear
DIP	Co(II)	EtOH–H_2O	3·7	0·59	0·58	not clear
	Ni(II)	H_2O	3·7	0·62	0·63	clear
		EtOH–H_2O	10·0	0·62	0·61	clear
	Cd(II)	EtOH–H_2O	4·5	3·35	3·33	not clear
		EtOH–H_2O	5·6	3·35	3·32	clear
		EtOH–H_2O	10·0	3·35	3·34	clear
	Ca(II)	H_2O	10·0	0·41	0·41	clear

* Aqueous ethanol.

The compound DAI was successfully applied to the titration of copper(II) in the pH range 3–8 but not to titrations of the other metals, owing to the weak colour reactions. With copper(II), the colour change in neutral solution was sharp, and heating or addition of ethanol was not necessary. In acid solution the colour change was not clear because of the increased absorption of the indicator in the visible region. As predicted theoretically, the titration was impossible in the presence of ammonia at a pH above 8 as a result of the weak stability of the copper(II)–DAI chelate. The colour change observed for DAI was reddish brown to yellow or orange–yellow, and this resembles that observed for DIP.

The compound IAM showed the clearest end-point, probably because the chelates of IAM are less stable than the chelates of IAN and DIP and the colour change from reddish violet to yellow seems to be more distinguishable than that from red or reddish brown to yellow, but its optimum pH ranges were found to be narrower than those of IAN.

Titrations in the presence of the copper(II)-EDTA chelate. Flaschka and Abdine[11] extended the applicability of PAN as an indicator by using it in the presence of copper(II)-EDTA. It was found that by a similar procedure the azoimidazoles IAN, IAM and DIP could be applied to the titrations of such metals as do not show remarkable colour reactions with them, because, as reported in the preceding paper,[1] they form highly coloured, stable copper chelates ($\log K_{\mathrm{ML}} = 13{\cdot}3$–$14{\cdot}5$). Thus, calcium(II) was titrated successfully in the pH range 8–10 and the titration of cadmium(II) was possible at pH values as low as 5·6. Although it was impossible to titrate cobalt(II) without addition of copper(II)-EDTA, it could be titrated by this method with a sharp colour change. The results are summarized in Table III.

The compound DAI, which forms only a weak copper chelate ($\log K_{\mathrm{ML}_1} = 5{\cdot}0$ and $\log K_{\mathrm{ML}_2} = 6{\cdot}4$), was not usable for this titration procedure.

Diagrams for prediction of titration error and sharpness of colour change

Although detailed estimations of the colour change may be made by calculating x from equations (11) and (12), it would be more convenient if the colour change could be estimated from a diagram without lengthy calculations. Ringbom[12] constructed a convenient diagram, from which the error dependent on the precision of end point-detection can be obtained. The titration error is expressed as the difference between x at the end-point and the equivalence point. Attempts were therefore made to construct diagrams for prediction of titration errors and sharpness of colour changes for indicators forming only ML complexes.

By using the conditional constants, K_{MY}' and K_{ML}', the error E and the sharpness $\mathrm{d}y/\mathrm{d}x$ can be expressed as follows.[2–4]

$$E = \frac{yK_{\mathrm{ML}}'}{K_{\mathrm{MY}}'}\left(\frac{1}{1-y} - \frac{C_{\mathrm{L}}}{C_{\mathrm{M}}}\right) - \frac{1}{C_{\mathrm{M}}K_{\mathrm{MY}}'} - \frac{1-y}{y}\,\frac{1}{C_{\mathrm{M}}K_{\mathrm{ML}}'} - \frac{C_{\mathrm{L}}}{C_{\mathrm{M}}}(1-y) \tag{17}$$

$$\frac{\mathrm{d}y}{\mathrm{d}x} = 1\Bigg/\left[\frac{C_{\mathrm{L}}}{C_{\mathrm{M}}} + \frac{1}{y^2C_{\mathrm{M}}K_{\mathrm{ML}}'} + \frac{K_{\mathrm{ML}}'}{K_{\mathrm{MY}}'}\left\{\frac{1}{(1-y)^2} - \frac{C_{\mathrm{L}}}{C_{\mathrm{M}}}\right\}\right]. \tag{18}$$

According to equation (17), the E values corresponding to various sets of $\log K_{\mathrm{ML}}'$ and $\log K_{\mathrm{MY}}'$ were calculated for $C_{\mathrm{M}} = 10^{-2}$–$10^{-3}M$. The plot of E against $\log K_{\mathrm{ML}}'$ with $\log K_{\mathrm{MY}}'$ as a parameter for $C_{\mathrm{M}} = 0{\cdot}002M$ and $C_{\mathrm{L}} = 0{\cdot}000025M$ is shown in Fig. 6. The $\mathrm{d}y/\mathrm{d}x$ values were analogously calculated from equation (18) by varying $\log K_{\mathrm{MY}}'$ and $\log K_{\mathrm{ML}}'$. The plot of $\mathrm{d}y/\mathrm{d}x$ against $\log K_{\mathrm{ML}}'$ with $\log K_{\mathrm{MY}}'$ as a parameter for the same set of C_{M} and C_{L} is shown in Fig. 7.

From these diagrams the titration error and the sharpness of the colour change of an indicator may be estimated, if $\log K_{\mathrm{MY}}'$ and $\log K_{\mathrm{ML}}'$ are known. In general, the colour change is expected to be very sharp when $\log \mathrm{d}y/\mathrm{d}x > 2$, whereas it would be slow when $\log \mathrm{d}y/\mathrm{d}x < 1{\cdot}5$. For example, $\log K_{\mathrm{ML}}'$ of copper(II)-IAN is 5·8 and $\log K_{\mathrm{MY}}'$ of copper(II)-EDTA is 10·1 at pH 4·0 (0·1M acetate buffer); hence, E and $\log \mathrm{d}y/\mathrm{d}x$ are found from Figs. 6 and 7 to be $-0{\cdot}2\%$ and 1·9, respectively.

Comparison of the predicted colour changes with the experimental results

Although the limits of the useful pH ranges of the azoimidazoles were not strictly investigated, the experimental findings about their use were usually explained by the theoretical calculations. For example, the slow colour change after the end-point observed for the nickel(II)–IAN system at pH > 9 could be predicted by the values $E > 1\%$ and $\log dy/dx < 1$. The compound DAI could not be used for copper(II) at pH > 8 in the presence of ammonia, and this fact corresponds well with the E and $\log dy/dx$ values calculated theoretically.

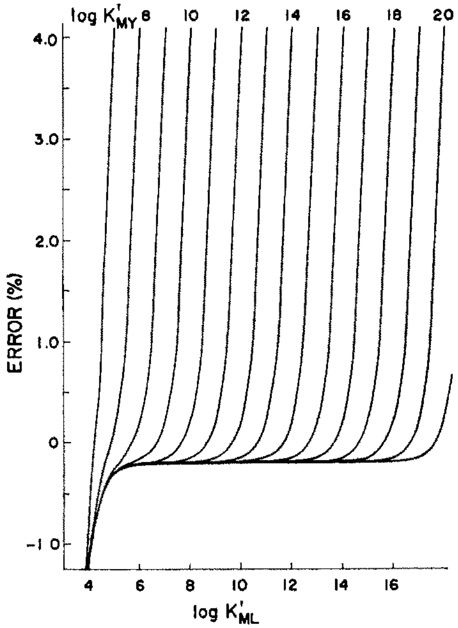

FIG. 6.—Error(%) at $y = 0{\cdot}8$ plotted against $\log K_{ML}'$ with $\log K_{MY}'$ as a parameter. $C_M = 0{\cdot}002M$, $C_L = 0{\cdot}000025M$.

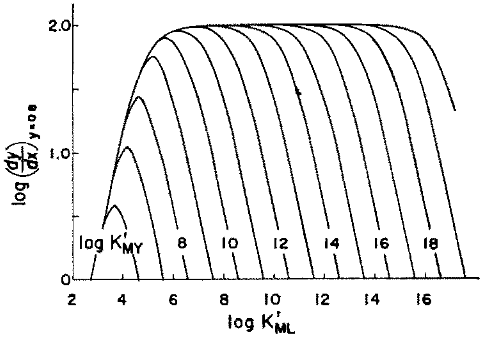

FIG. 7.—Sharpness at $y = 0{\cdot}8$ plotted against $\log K_{ML}'$ with $\log K_{MY}'$ as a parameter. $C_M = 0{\cdot}002M$, $C_L = 0{\cdot}000025M$.

However, the pH ranges for the zinc(II)–IAN, cadmium(II)–IAN and cadmium(II)–DIP systems were found to be narrower than those calculated theoretically; in acid or neutral solution the colour developments were weak and the colour changes were not clear. Many factors are considered to affect the colour change at the end-point, but, in the present cases, one of the reasons for the difference between the predicted pH ranges and the experimental ones may be that the stabilities of the metal–indicator chelates in the solution being titrated are not properly expressed by the stability constants determined in 50% v/v dioxan–water at constant ionic strength (0·1*M* potassium nitrate).

CONCLUSION

The experimental results for the pH ranges and the sharpness of the colour changes are approximately consistent with those predicted theoretically. It is apparent from the results that the azoimidazoles are useful indicators for a variety of metal ions. The observed sharp colour changes at the end-point can be explained in terms of the stabilities of the metal-indicator complexes. If the complexes are too stable or too labile as compared with the EDTA chelates, the colour changes will not be sharp. The investigations of Reilley and Schmid[4] and the present calculations indicate that $\log K_{MY}'/K_{ML}' = 4$ is a favourable condition for a sharp colour change for an indicator forming a 1:1 complex, and this is the case with the copper chelates of IAN, IAM and DIP.

However, it must be mentioned that the theoretical treatment does not take into account such factors as the reaction rates and that the constants used in the calculations may be affected by the conditions of titrations. Nevertheless, the calculations will be of value in studying the usefulness of a compound as a metallochromic indicator.

Acknowledgement—The authors are grateful to the members of Kyoto University Computation Center for computations.

Zusammenfassung—Die Anwendbarkeit von mehreren Azoimidazolen als Metallfarbindikatoren wurden im Lichte der allgemeinen, die Farbänderungen bei visuellen chelatometrischen Titrationen ausdrückenden Gleichungen untersucht. Mit Hilfe der Stabilitätskonstanten der Chelate mit Nickel(II), Kupfer(II), Zink(II) und Cadmium(II) wurden die richtigen pH-Bereiche, Titrationsfehler und die Schärfe der Farbänderungen theoretisch vorhergesagt und der Nutzen dieser Reagentien als Indikatoren experimentell bestätigt. Auch das System Kupfer(II)-EDTA-Indikator wurde experimentell untersucht. Mit den OH enthaltenden Azoimidazolen konnten Kupfer, Nickel, Zink, Cadmium, Blei und Wismut direkt titriert werden, Calcium und Kobalt in Gegenwart von Cu(II)-EDTA. Es wurde versucht zur Ermittlung der Titrationsfehler und der Schärfe der Farbumschläge graphische Darstellungen zu konstruieren.

Résumé—On a étudié les possibilités d'application de plusieurs azoimidazoles comme indicateurs métallochromes à la lumière des équations générales exprimant le changement de coloration dans les titrages chélatométriques visuels. En utilisant les constantes de stabilité des chélates de nickel(II), cuivre(II), zinc(II) et cadmium(II), les domaines de pH utiles, les erreurs de titrage et la netteté des changements de coloration ont été prédits théoriquement et l'utilité de ces réactifs comme indicateurs a été établie expérimentalement. On a aussi examiné expérimentalement le système Cu(II)–EDTA-indicateur. Les azoimidazoles contenant OH ont pu être appliqués aux titrages directs des cuivre, nickel, zinc, cadmium, plomb et bismuth et aux titrages du calcium et du cobalt en présence de Cu(II)–EDTA. Des tentatives ont été faites pour construire des diagrammes pour l'estimation des erreurs de titrage et de la netteté des changements de coloration.

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SHORT COMMUNICATIONS

New chromogens of the ferroin-type—I. Substituted triazines related to 6-cyano-2,2′-bipyridine

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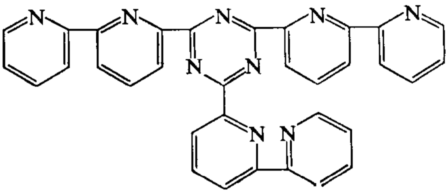
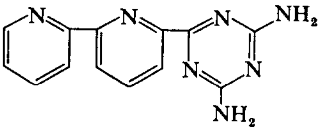
CHROMOGENS of the ferroin type are distinguished structurally by the presence of the bidentate chelate functional group $-N{=}\overset{|}{C}-\overset{|}{C}{=}N-$, commonly referred to as the ferroin reacting group or the methine chromophore. The first and best known examples are 1,10-phenanthroline and 2,2′-bipyridine. The ability of these compounds to form intensely coloured iron(II) and copper(I) chelates has prompted extensive investigation, particularly with respect to finding improved colorimetric reagents for iron and copper.[1] Many such compounds have been synthesized[2] and studied.[3] Some of the more outstanding iron chromogens found to date are 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline),[4,5] 2,4,6-tripyridyl-1,3,5-triazine (TPTZ),[6,7] and 5,6-diphenyl-3-(4-phenyl-2-pyridyl)-1,2,4-triazine (PPDT).[8,9] For copper, the most sensitive specific chromogenic reagent found to date is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine).[10,11]

The search for superior chromogenic reagents of the ferroin type continues. Professor F. H. Case of Temple University recently reported the synthesis of a variety of substituted triazines related to 6-cyano-2,2′-bipyridine.[12] Spectrophotometric data for the iron(II), copper(I), and cobalt(II) chelates of these are reported here. The new chromogens are identified below by name and structure.



2,4,6-Tris(2,2′,6-bipyridyl)-1,3,5-triazine (I)



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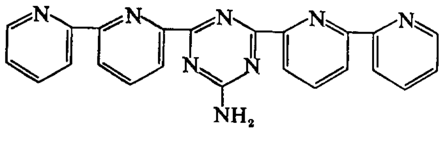
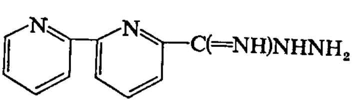
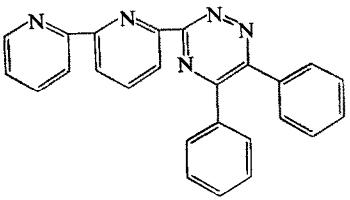


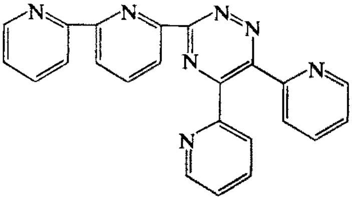
2-Amino-4,6-tris(2,2′,6-bipyridyl)-1,3,5-triazine (III)



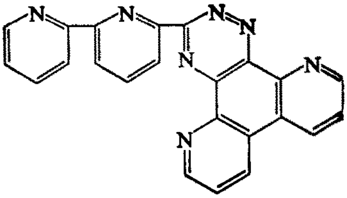
2,2′-Bipyridine-6-carbohydrazide imide (IV)



3-(2,2′,6-Bipyridyl)-5,6-diphenyl-1,2,4-triazine (V)



3-(2,2′,6-Bipyridyl)-5,6-bis(2-pyridyl)-1,2,4-triazine (VI)



3-(2,2′,6-Bipyridyl)-1,2,4-triazino[5,6-*f*][4,7]-phenanthroline (VII)

EXPERIMENTAL

Reagents

Samples of the seven new chromogens investigated were provided by Dr. Francis H. Case of Temple University. Analytical and preparative details have been reported elsewhere.[12]

Standard solutions of metal ions were prepared by weight so that weighed samples could be used. The standard iron solution contained 0·1220 mg of iron per g and was prepared from pure iron wire and a slight excess of hydrochloric acid. Standard copper sulphate solution containing 0·1605 mg of copper per g was prepared by dissolving the pure metal in nitric acid, fuming with sulphuric acid, cooling, and adding water to give a known concentration. The standard cobalt solution, prepared from pure $CoCl_2 \cdot 6H_2O$, contained 0·2976 mg of cobalt per g.

Buffers of pH from 0 to 2 were 1*M* potassium chloride solutions with sufficient hydrochloric acid added to give the required pH. Buffers of pH from 3 to 6 were prepared from acetic acid and sodium acetate with a total acetate concentration approximately 1*M*. Buffers of pH from 6·7 to 7·3 were 1*M* ammonium acetate solutions adjusted to the required pH. Buffers of pH from 8 to 10 were prepared from ammonium chloride and ammonia solution with a total concentration of ammonium species approximately 1*M*. Ammonia solutions were used as buffers of pH from 10 to 11·4. For pH 12 and higher, sodium hydroxide solutions were used.

A 10% solution of iron-free hydroxylamine hydrochloride was prepared by the procedure of Smith, McCurdy, and Diehl.[5]

Solutions (0·005*M*) of the chromogens were prepared by dissolving weighed amounts in ethanol-water mixtures (1 + 1). In most cases a drop or more of concentrated hydrochloric acid was added to dissolve the reagent. Chromogen V was dissolved in ethanol without acid, and VII was dissolved in dilute hydrochloric acid without ethanol.

Complex formation and extraction studies

To each of a series of test-tubes, containing 5 drops of standard metal solution, 2 drops of hydroxylamine hydrochloride solution, and 10 drops of a different buffer (to cover the pH range 0–12), were added 5 drops of the complexing agent solution. The pH range over which complexation occurred, as indicated by colour formation, was noted, and so was the pH range for which colour formation was maximal. If precipitation occurred, ethanol was added to dissolve the precipitate before evaluation of the colour. The extractability of the complex with isoamyl alcohol was determined for those solutions to which ethanol was not added.

Absorption characteristics

Solutions of the various complexes were prepared for spectrophotometric examination as follows: a weighed quantity of standard metal ion solution was delivered into a 10-ml volumetric flask from a weight burette; 1 ml of iron-free hydroxylamine hydrochloride solution, 2 ml of the chromogen solution, and 2 ml of an appropriate buffer were added in that order; the contents of the flasks were diluted to volume with ethanol (water in the case of Chromogen VII).

Absorption spectra in the visible region were recorded with a Cary Model 14 spectrophotometer. All solutions, including blanks, were measured *vs.* water.

RESULTS

None of the new compounds tested proved to be superior to existing ferroin type chromogens, either with respect to sensitivy or selectivity. Nevertheless, the results merit reporting for general interest and to preclude repetition by others.

Most of the results are summarized in Table I. The wavelengths given are for maximum absorbance unless otherwise specified. Molar absorptivity values (ε) correspond to the wavelengths cited. Extractability into isoamyl alcohol is generally nil, with only a few exceptions. In several instances the colours of the chelates faded noticeably during the spectral measurements. Colour stability is poor for the iron(II) chelates of chromogens I and VI and for the cobalt(II) chelate of chromogen VII.

The new chromogens form only pale yellow or orange complexes with nickel(II). Chromogen VII is the most sensitive of the seven for nickel; in aqueous solutions of pH 2–7, its nickel(II) complex exhibits an absorption band (shoulder) at 430 mμ, with a molar absorptivity of 300.

The identities of the iron(II) chelates were examined by the mole-ratio method. Chromogens IV, V, VI and VII form very stable chelates with iron(II) in aqueous ethanol solutions. Mole-ratio plots for these show essentially no curvature, but sharp intersections corresponding to a ligand to metal ion combining ratio of 2 : 1. Chromogens I, II and III apparently form both 1 : 1 and 2 : 1 ligand : metal

TABLE I.—PROPERTIES OF THE METAL CHELATES

Metal ion	Chromogen	Chelate colour	pH Range for max. colour	Extractability	λ, mμ	ε
Fe^{2+}	I	violet	7–10	nil	556	6400
	II	violet	4–9	nil	557	9100
	III	violet	4–5	partial	540	1500
	IV	red	4–8	nil	550	8700
	V	blue	3–7	partial	590	12500
	VI	blue	3–6	partial	601	11900
	VII	blue	3–10	nil	660	12000
Cu^+	I	pale orange	9–11	nil	†	†
	II	orange	8–10	nil	427	2500
	III	orange	7–11	nil	448	2700
	IV	pale orange	4–7	nil	†	†
	V	orange-brown	7–9	quantitative	470*	2900*
	VI	orange-brown	7–11	nil	450	3400
	VII	purple	5–8	nil	540*	2400*
Co^{2+}	I	pale yellow	9–11	nil	†	†
	II	pale yellow	11–14	nil	440*	100*
	III	pale yellow	8–11	nil	425*	300*
	IV	gold	11–14	nil	510*	300*
	V	orange-brown	1–11	quantitative	544	2600
	VI	gold	8–11	nil	555	2700
	VII	orange	9–11	nil	579	3100

* Shoulder.

† Absorption characteristic not appreciably different from that of chromogen.

iron(II) species, of only moderate stability. Their mole-ratio plots are ʃ-shaped with considerable curvature in the vicinity of both 1:1 and 2:1 ligand to iron ratios.

The iron(II) chelates of chromogens I and III are less stable and exhibit much lower molar absorptivities than the others. Presumably steric factors are responsible. Molecular models indicate that only three nitrogen donor atoms in these multi-pyridine type ligands can coordinate equatorially to octahedral iron(II) without severe strain. Moreover, the fourth and fifth uncoordinated pyridine rings can clash with a second multidentate ligand, causing them to twist out of coplanarity with the coordinated portion, so that the transition moment and molar absorptivity are less than expected. Stability should also suffer. Similar results and interpretations have been reported for the analogous iron(II) chelates of 2,2′,2″, 2‴-quaterpyridine.[13] Regardless of cause, the results clearly indicate that no beneficial purpose is served in designing new ferroin chromogens by extending the ferroin grouping beyond that of a tridentate functionality.

Acknowledgement—This investigation was supported by a grant from the G. Frederick Smith Chemical Company, and the compounds were provided by Dr. Francis H. Case.

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Summary—A spectrophotometric study has been made of the iron(II), cobalt(II), nickel(II) and copper(I) chelates of seven new compounds that contain the ferroin functional grouping. None of the new compounds proved to be superior to chromogenic reagents currently in use, but the results are of interest in designing new chromogens.

Zusammenfassung—Die Chelate sieber neuer, die funktionelle Gruppe des Ferroins enthaltender Verbindungen mit Eisen(II), Kobalt(II), Nickel(II) und Kupfer(I) wurden spektrophotometrisch untersucht. Keine der neuen Verbindungen erwies sich den zur Zeit gebräuchlichen farbbildenden Reagentien überlegen, doch sind die Ergebnisse von Interesse für die Entwicklung neuer Farbbildner.

Résumé—On a effectué une étude spectrophotométrique des chélates de fer(II), cobalt(II), nickel(II) et cuivre(I) avec sept nouveaux composés contenant le groupe fonctionnel ferroïne. Aucun de ces nouveaux composés ne s'est révélé être supérieur aux réactifs chromogènes couramment utilisés, mais les résultats sont intéressants pour la conception de nouveaux chromogènes.

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Improvement of iron determination by use of ferroin–organic dye ion-association complexes

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Summary—Extraction of ion-associates of tris(1,10-phenanthroline)-iron(II) cation with monosulphonated azo dye anion into 1,2-dichloroethane is described. The method increases the sensitivity of the colorimetric determination of bivalent iron with 1,10-phenanthroline.

THE reaction of iron(II) with 1,10-phenanthroline to form ferroin [Fe(phen)$_3^{2+}$], discovered by Blau,[1] has found wide application.[2-4] The complex shows maximum absorption at 508 mμ, with molar absorptivity[5] 11·1 × 10^3. A shortcoming of this reaction is the insolubility of the complex cation in organic solvents, but some of its ion-association complexes [Fe(phen)$_3$]X$_2$ where X is a univalent anion, are extractable by suitable organic solvents and may be used for extractive photometric determination of iron or of the associated anions.

So far, investigation has been confined to the ion-association complexes with colourless inorganic anions, such as ClO_4^-, I^-, SCN^-, CN^-, BF_4^-, and with some organic anions such as pentachlorophenolate, trichloroacetate and dioctylsulphosuccinate.

During a study of the extraction of ferroin perchlorate[6] it was verified that the extraction yield is influenced by the anion concentration and by the dielectric constant of the solvent used. On the basis of these facts and the work of West and co-workers,[7-9] on the ternary complexes of [Ag(phen)$_2$]$^+$ and [Cu(phen)$_2$]$^{2+}$ with Bromopyrogallol Red and Rose Bengal Extra, we concluded that it might be possible to use organic dyes with ferroin to improve the sensitivity of iron determination.[10]

Attention was directed to dyes soluble and ionizable in water, as the anionic form of the dye is necessary for formation of the ion-association complex, and the sulphonated azo dyes seemed the most suitable. Orange or red dyes were considered first because it was assumed that the sensitivity would be increased most if the absorption maximum of the dye was close to that of ferroin.

EXPERIMENTAL

Procedure

In a separatory funnel 5 ml of 5 × 10^{-5} *M* iron(II) ammonium sulphate, 0·1 ml of 10% hydroxylamine hydrochloride solution, 5 ml of 5 × 10^{-4} *M* 1,10-phenanthroline and 5 ml of 10% sodium acetate solution were mixed with 2·5 ml of 1 × 10^{-3} M solution of organic dye and diluted with water to 25 ml. This solution was extracted three times with 8-ml portions of 1,2-dichloroethane. The combined extracts were diluted to 25 ml and centrifuged, and then the absorption spectrum was measured with 1,2-dichloroethane as reference. A blank was run on solutions which contained all the components except iron, to allow for extraction of dye itself.

In Fig. 1 the absorption spectra of 1,2-dichloroethane extracts of Orange III (C.I. 13025), Orange II (C.I. 15510), Acid Red 88 (C.I. 15620), Acid Orange 8 (C.I. 15575), Acid Orange 19 (C.I. 14690)[11] are shown, corrected for the blank, which in most cases did not exceed 10% of the absorbance of the ion-association complexes. For comparison the absorption spectrum of an aqueous ferroin solution is also shown.

DISCUSSION

From the absorption spectra it can be seen that the organic dye anions form extractable ferroin complexes which increase the sensitivity for iron determination. It is of interest that only monosulphonated dyes are suitable. In the case of dyes with more sulphonic acid groups, such as Direct Red 2 (C.I. 23500), Trypan Red (C.I. 22850), Acid Orange 10 (C.I. 16230), Acid Violet 7 (C.I. 18055),[11] extraction under the conditions described was not observed.

From Fig. 1 it is evident that the sensitivity is increased most by the use of Orange III. The associated dyestuff enhances the absorbance of the ferroin but the resulting absorption spectrum cannot be derived by simple addition of the ferroin and dyestuff curves. Comparisons between the absorption maxima of aqueous solutions of the dyestuffs and of 1,2-dichloroethane solutions of the ferroin complexes of these dyes are given in Table I.

These ferroin-dyestuff complexes can be used only in weakly acidic or weakly alkaline solutions. In strongly acidic medium 1,10-phenanthroline is protonated and forms an ion-association complex

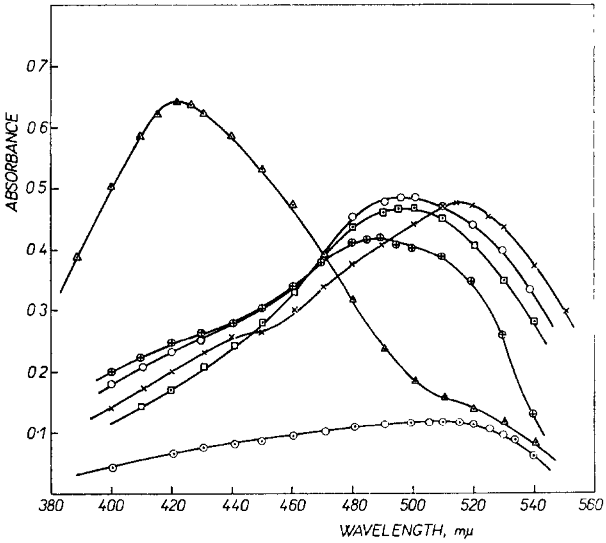

FIG. 1.—Absorption spectra of 1,2-dichloroethane solutions of ferroin ion-association complexes with anions of monosulphonated azo dyes and aqueous ferroin solution.
△—Orange III, C. I. 13025
⊕—Orange II, C. I. 15510
○—Acid Orange 8, C. I. 15575
×—Acid Red 88, C. I. 15620
⊡—Acid Orange 19, C. I. 14690
○—1,10-phenanthroline
1 cm cuvettes—UNICAM SP 600

Table I.—Absorption maxima of the dyestuffs and their ferroin ion-association complexes

Dyestuff	Absorption maximum Water solution of the dyestuff, mμ	 1,2-dichloroethane solution of association complex, mμ
Orange III	464	423
Orange II	488	488
Acid Orange 8	495	495
Acid Orange 19	490	502
Acid Red 88	510	516

with the anion of the dye, and this complex is also extracted into 1,2-dichloroethane. The selectivity of the reaction probably decreases because one may expect formation of ion-association complexes with colourless 1,10-phenanthroline cationic complexes such as those of zinc and cadmium.

In a similar way it should be possible to increase the sensitivity of colorimetric reactions of 1,10-phenanthroline derivatives, *e.g.*, 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline) and of other agents which form cationic complex with iron or other cations, *e.g.*, α,α-dipyridyl, tripyridyl-s-triazine, terpyridyl.

The main advantage of the method is the improvement in sensitivity of photometric determination of iron by use of readily available and substantially cheaper reagents.

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Zusammenfassung—Es wird die Extraction des Ionenassoziaten des Tri(1,10-Phenanthrolin)-Eisen(II)-Kations mit Anionen der monosulfonisierten Azo-Farbstoffen in 1,2-Dichloräthan Beschrieben. Die Methode erhöht die Empfindlichkeit der kolorimetrischen Reaktion des Zweiwertigen Eisens mit 1,10-Phenanthrolin.

Résumé—On décrit l'extraction des associations ioniques du tris(1,10-phénanthroline)fer(II) cation avec des anions des azocolorants monosulphonés par le 1,2-dichloroethane. La méthode augments la sensibilité de la reaction colorimétrique du fer(II) avec le 1,10-phénanthroline.

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ANNOTATION

Application of 2-diphenylacetyl-1,3-indandione chemistry in the identification of organic compounds

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It has been found that 2-diphenylacetyl-1,3-indandione-1-hydrazone (**1**) is a valuable reagent for identifying and characterizing carbonyl compounds.[1] Aldehydes and ketones react with **1** to give fluorescent azines. Brandt and Cheronis[2] showed that spectrofluorimetric methods are useful in detecting concentrations of these azines as low as 10^{-9} *M*.

Because many derivatives of **1** are highly crystalline, fluoresce brilliantly and have intense visible colours, we wish to point out the potential of using 2-diphenylacetyl-1,3-indandione and its closely related analogues as reagents in the identification of various classes of organic compounds. Scheme 1 summarizes a detailed investigation by Bechara on the preparation of fluorescent derivatives of 2-diphenylacetyl-1,3-indandione.[3] Potential usefulness in qualitative analysis is given in Table I.

TABLE I.—POTENTIAL USEFULNESS OF 2-DIPHENYLACETYL-1,3-INDANDIONES IN THE IDENTIFICATION OF ORGANIC COMPOUNDS

Compound to be identified	Reagent	Reaction conditions	Product (Scheme 1 compound no.)
aldehyde, ketone	1	$CHCl_3$, H^+, reflux	see Ref. 1
ortho-ester	1	C_2H_5OH, *p*-toluenesulphonic acid, reflux	2
primary amine (excess)	2	C_2H_5OH, reflux	4
primary amine (equiv)	2	C_2H_5OH, reflux	8
secondary amine	2	alcohol, reflux	6
alcohol	2	alcohol, reflux	7
acyl or anhydride (excess)	1	pyridine, $(C_2H_5)_2O$, reflux	18
acyl or anhydride (equiv)	1	pyridine, benzene, reflux	5
cyclic anhydride	1	pyridine, benzene, reflux	17
ester	1	$NaOCH_3$, excess of ester, reflux	16
primary amine	1	C_2H_5OH, reflux	4
primary amine	3	C_2H_5OH, reflux	4
hydrazine (excess)	3	CH_3OH, reflux	15
substituted hydrazine (excess)	3	H_2O, reflux	14
substituted hydrazine	3	CH_3OH, reflux	13
acid hydrazide	3	$CHCl_3$, reflux	9
alkylating agents	10	CH_3OH, reflux	11, 12

The data in Table I show the reaction conditions for particular examples studied by Bechara. Only classes of compounds which were actually examined are listed. However, additions can readily be made. For example, compound **1** would also be expected to react with alkylating agents. A *trans*-esterification, using compound **2**, might be applicable to a great variety of esters. With Scheme 1, esters were detected readily (reactions 1–16) only if there was a strong electron-withdrawing inductive effect on the ester carbonyl.

The potential usefulness of 2-diphenylacetyl-1,3-indandione chemistry in the identification of organic compounds centres around compounds **1**, **2** and **3**[*] (Scheme 2). Though reaction conditions

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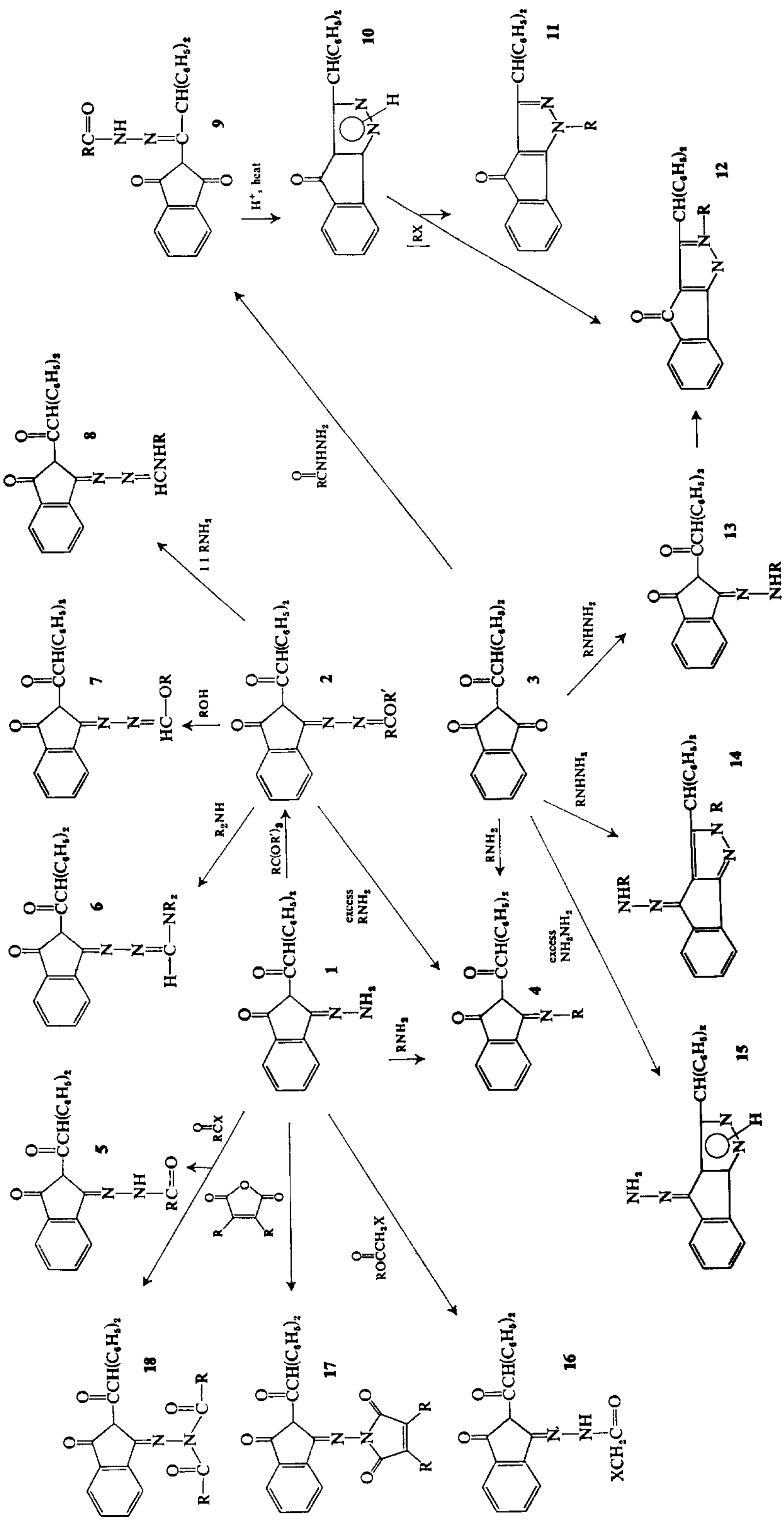
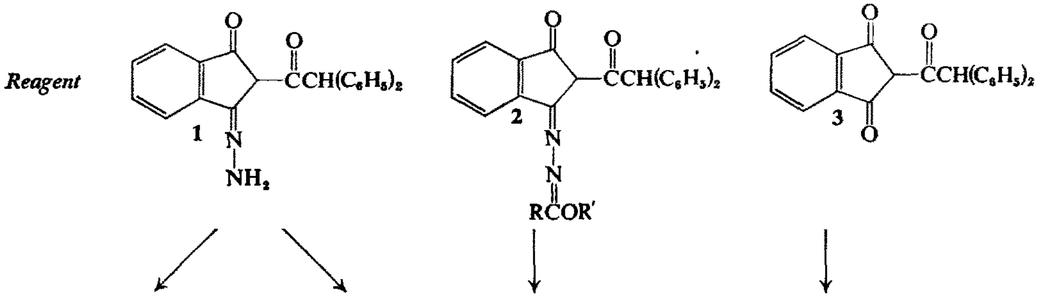
[*] Compounds **1** and **3** are available commercially from the Nease Chemical Company, State College, Pennsylvania. The preparation of compound **2** is described in reference 3.



Scheme 1
Preparation of 2-diphenyl-1,3,-indandione derivatives.



Reaction conditions	benzene pyridine reflux	alcohol acid reflux	alcohol reflux	alcohol reflux
Compounds identified	acyl anhydride ester primary amine	aldehyde ketone ortho-ester	primary amine secondary amine alcohol	primary amine hydrazide substituted hydrazide acid hydrazide

Scheme 2

Identification of organic compounds by use of 2-diphenyl-1,3-indandione chemistry.

preclude the use of compounds **1**–**3** in any detection application, we consider that the chemistry can be exploited to provide the analytical chemist with derivatives from a variety of functional groups. These derivatives can be differentiated easily by thin-layer chromatography, fluorimetry, and/or absorption spectroscopy. An example follows (compound 13, Scheme 1) of the application of reagent 3 in the preparation of derivatives of hydrazines.

A mixture of 2·0 g (0·0056 mole) of 2-diphenylacetyl-1,3-indandione, 1·0 ml of phenylhydrazine and 50 ml of methanol was refluxed for 4 hr. The solution was concentrated to half its volume and cooled in a refrigerator. The yellow solid that precipitated was isolated and recrystallized from methanol to give 1·95 g (81%) of the product 2-diphenylacetyl-1,3-indandione-1-phenylhydrazone (m.p. 173°; C, 81·0%; H, 5·2%; N, 6·5%: $C_{29}H_{22}N_2O_2$ requires C, 80·93%; H, 5·12%; N, 6·51%).

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Summary—Derivatives of 2-diphenylacetyl-1,3-indandione have proved useful in identification of a wide variety of functional groups in organic compounds, and an account is given of their application in qualitative analysis.

Résumé—Des dérivés de la 2-diphénylacétyl 1,3-indandione se sont révélés utiles pour l'identification d'une grande variété de groupes fonctionnels dans les composés organiques et l'on donne un rapport de leur application en analyse qualitative.

Zusammenfassung—Derivate von 2-Diphenylacetyl-1,3-indandion haben sich bei der Identifikation einer großen Anzahl funktioneller Gruppen in organischen Verbindungen als nützlich erwiesen; ihre Anwendung bei der qualitativen Analyse wird abgehandelt.

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LETTERS TO THE EDITOR

Determination of sodium in hen egg yolk

SIR,

Most of the methods proposed for determination of the sodium content of hen egg yolk are based on determining the chloride present and equating this stoichiometrically with the sodium content. Direct determination of sodium by flame photometry is unreliable unless the yolk is first ashed, because the atomizer easily becomes blocked with chalazae. The ashing is difficult and makes routine determinations tedious. We therefore tried using a sodium-sensitive glass electrode for direct potentiometric measurement of the sodium content, and found it gave reliable results and provided a rapid routine method.

A calibration curve is prepared as follows. Take about 1 kg of yolk known to be of low sodium content, mix it thoroughly in an emulsifying mixer, and withdraw a sample of 50–60 ml. To the rest add 0·5 g of dried sodium chloride, mix again and take another sample of about the same size. Repeat this set of operations until a total of 5 g of salt has been added. Determine the chloride content of each sample by Hubach's potentiometric method;[1] the increase in chloride content is equivalent to the increase in sodium content. The sodium content of the original yolk is taken, for routine purposes, as equivalent to the chloride content, but for accurate work should be determined directly. (This procedure is necessary because on the laboratory scale it is not always possible to guarantee complete mixing, and some salt remains undissolved at the bottom of the vessel, presumably because of the rheological properties and high viscosity of egg yolk.) Standardize the pH meter with $0{\cdot}1M$ sodium chloride, measure the potentials of each of the prepared samples *vs.* a calomel electrode, and plot a calibration curve. Determine the sodium content of routine samples from the potentials and the calibration curve.

The electrodes must be thoroughly washed and stored in $0{\cdot}1M$ sodium chloride between determinations. The potential of the sodium electrode is affected by a pH less than 7, but fresh yolk usually has a $\mathrm{pH} > 7$ and $\mathrm{pNa} < 2$ so the effect is not significant. Comparatively large variations in total salt content do not affect the potential within the limits of error reported.

Repeated analysis (6 determinations) of the same sample gave an average sodium chloride content of 0·40% (standard deviation 0·014%) by the potentiometric chloride method and 0·37% (standard deviation 0·019%) by the direct method described here. Analysis of 15 samples by both methods gave agreement within experimental error between the results based on chloride and those based on sodium. This seems to imply that either method is satisfactory for routine determination of the "natural salt" content of egg yolk, but that in research on feed and metabolism factors it might be desirable to use both together. The sodium-electrode method is very rapid and most suitable for process control.

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8 October 1967

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The masking coefficient in precipitation reactions

SIR,

Kelly and Sutton[1] recently reported that for a salt M_jA_i with solubility product K, the masking coefficient in the presence of a complexing agent and a large excess of precipitating agent could be calculated from the equation.

$$\mathrm{pM}' = \frac{1}{j}\,(\mathrm{p}K + i\log[\mathrm{A}']) - \frac{i}{j}\log \alpha_{\mathrm{A(H)}} - \log \alpha_{\mathrm{M}} \qquad (1)$$

where pM′, the masking coefficient, is the negative logarithm of the total concentration of metal predicted to remain in solution and α_A and α_M are the side-reaction coefficients for the precipitating anion and metal respectively; since a large excess of precipitating agent is added, the initial concentration (C_A) can replace the total concentration of it, [A′], remaining in solution.

If the only side-reaction of the metal to be considered involves the formation of a 1:1 complex with the chelating ligand (as with EDTA, H_4Y)

$$\alpha_{\mathrm{M}} = 1 + \frac{K_{\mathrm{MY}}[\mathrm{Y}']}{\alpha_{\mathrm{Y(H)}}} \qquad (2)$$

where [Y′] is the concentration of all complexing ligand other than that involved in reaction with the metal and $\alpha_{Y(H)}$ is the side-reaction coefficient for the complexing agent. C_Y, the initial concentration of complexing agent, can replace [Y′] in equation (2) only if the amount of MY formed is negligible compared to the amount of complexing agent; this will be true if there is a large excess of complexing agent or if no metal side-reaction is taking place. In the experiments reported by Kelly and Sutton, where equimolar amounts of metal and complexing reagent were mixed, the use of C_Y instead of [Y′] results in an error of only 0·1 pM units if 20% of Y is used for masking. As the masking effect increases, however, the error in calculation becomes significant; at 90% use of Y for masking the error is 1 pM unit, and if nearly all of it is used (say 99·9%) the error is 3 pM units. When C_Y cannot be substituted for [Y′], then [Y′] can be calculated as follows.

Since $[\mathrm{Y}'] = C_Y - [\mathrm{MY}]$ and $[\mathrm{MY}] = [\mathrm{M}][\mathrm{Y}]K_{\mathrm{MY}}$, then for the simplest case, where $i = j$

$$\begin{aligned}[\mathrm{MY}] &= \frac{K[\mathrm{Y}']}{[\mathrm{A}]\,\alpha_{\mathrm{Y(H)}}}K_{\mathrm{MY}} \\ &= \frac{KK_{\mathrm{MY}}\,\alpha_{\mathrm{A(H)}}\,[\mathrm{Y}']}{C_{\mathrm{A}}\,\alpha_{\mathrm{Y(H)}}} \qquad (3)\end{aligned}$$

and

$$\begin{aligned}[\mathrm{Y}'] &= C_{\mathrm{Y}} - \frac{KK_{\mathrm{MY}}\,\alpha_{\mathrm{A(H)}}\,[\mathrm{Y}']}{C_{\mathrm{A}}\,\alpha_{\mathrm{Y(H)}}} \\ &= \frac{C_{\mathrm{A}}C_{\mathrm{Y}}\,\alpha_{\mathrm{Y(H)}}}{C_{\mathrm{A}}\,\alpha_{\mathrm{Y(H)}} + KK_{\mathrm{MY}}\,\alpha_{\mathrm{A(H)}}}. \qquad (4)\end{aligned}$$

Substitution for [Y′] in equation (2) gives

$$\alpha_{\mathrm{M}} = 1 + \frac{K_{\mathrm{MY}}\,C_{\mathrm{A}}C_{\mathrm{Y}}}{C_{\mathrm{A}}\,\alpha_{\mathrm{Y(H)}} + KK_{\mathrm{MY}}\,\alpha_{\mathrm{A(H)}}}. \qquad (5)$$

At pH values where masking agents such as EDTA are useful (*i.e.*, if any appreciable masking occurs), the second term of equation [5] is large compared to unity, and the amount of metal remaining in solution can be calculated from the equation

$$\mathrm{pM}' = \mathrm{p}K - \log \alpha_{\mathrm{A(H)}} - \log K_{\mathrm{MY}} - \log C_{\mathrm{Y}} + \log\,(C_{\mathrm{A}}\,\alpha_{\mathrm{Y(H)}} + KK_{\mathrm{MY}}\,\alpha_{\mathrm{A(H)}}). \qquad (6)$$

For the salt M_jA_i,

$$\alpha_{\mathrm{M}} = 1 + \frac{K_{\mathrm{MY}}C_{\mathrm{Y}}C_{\mathrm{A}}^{i/j}}{C_{\mathrm{A}}^{i/j}\alpha_{\mathrm{Y(H)}} + K^{1/j}K_{\mathrm{MY}}\,\alpha_{\mathrm{A(H)}}^{i/j}}$$

and a general equation similar to (6) can be written.

These equations for α_M are always applicable; when the amount of MY formed is negligible compared to the amount of complexing agent, α_M is more easily determined since [Y′] is C_Y. At low pH values, although masking is still effective if K_{MY} is large enough, there is little masking for most metal ions and α_M approaches unity.

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THE ROLE OF 70–80% PERCHLORIC ACID AS OXYGEN DONOR AND THE OXIDATION POTENTIALS MADE AVAILABLE

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Summary—A study has been made of the probable oxidation potentials provided by perchloric acid in the concentration range 70–80%. The effect of acid concentration and temperature on the oxidation of chromium, vanadium, cerium, and manganese has been investigated. Available oxidation potentials appear to be 2.0–2.1 V or higher. The monohydrate of perchloric acid, $HClO_4 \cdot H_2O$, containing 84.6% of perchloric acid, has been made commercially available and authorized for distribution by common carrier. It can be diluted to give acid concentrations from 73.6% (corresponding to $HClO_4 \cdot 2H_2O$) upwards. Perchloric acid mixed with sulphuric acid is equivalent to high concentrations of perchloric acid and can be used for dissolution of ores and destruction of organic matter.

AMONG the many analytical applications of perchloric acid the most important involve its activity as an oxygen donor. At concentrations below 50% and at temperatures of 50–60°, perchloric acid releases no oxygen. Iron dissolves to give iron(II) perchlorate; zinc also dissolves with evolution of hydrogen and formation of zinc perchlorate.

At concentrations of 65% acid ($HClO_4 \cdot 3H_2O$) or higher, perchloric acid at its boiling point (160°) readily releases oxygen. Cellulose is converted into carbon dioxide at a moderate rate,[1] the reaction being catalysed by a trace of vanadium. Cellulose is oxidized violently by hot 70% perchloric acid (b.p. 195°). The 69–70% acid at its boiling point is required to oxidize chromium(III) to chromium(VI). Perchloric acid at the concentration corresponding to its water azeotrope, 72·5%, at its boiling point (203°) begins to convert cerium(III) into cerium(IV). The dihydrate ($HClO_4 \cdot 2H_2O$, 73·6%) oxidizes cerium(III) at 183°.

A study of 73·6–80% or even more concentrated perchloric acid as oxygen donor has not previously been made in an analytical context. The present study gives a better understanding of the oxygen donor activity of perchloric acid in the wet oxidation of organic material.

EXPERIMENTAL

Preparation of highly concentrated perchloric acid

The azeotrope of perchloric acid, b.p. 203°, is prepared by concentration of the 68–70% acid, the first few per cent of distillate being discarded. This concentration operation is accompanied by evolution of some chlorine, which can be removed from the azeotrope by passage of a stream of air. There is no hazard involved.

The dihydrate of perchloric acid, $HClO_4 \cdot 2H_2O$, is prepared[2] by the distillation of the 70–72% acid at 6–7 mmHg pressure.

The anhydrous acid is prepared[3,4] by either of two procedures. The more convenient[4] involves the vacuum distillation of the 70–72·5% acid in the presence of anhydrous magnesium perchlorate. The anhydrous acid thus formed is collected as distillate in a cold trap immersed in solid carbon dioxide.

Since anhydrous perchloric acid is not stable at ordinary temperature for longer than 72–96 hr, it is converted into the 84·6% acid. This monohydrate ($HClO_4 \cdot H_2O$), better designated oxonium perchlorate OH_3ClO_4, (m.p. 49·90°) is obtained by mixing equimolar amounts of the dihydrate and the anhydrous acid. The shipment, by common carrier, of properly ampoule-encased oxonium perchlorate is authorized and this acid is thus available commercially.[5]

All of the various acid strengths (70–84·6%) employed in the present study were analysed by titration of small weighed samples with standard sodium hydroxide. The error of duplicate or triplicate tests was 1 ppt or less. Acid concentrations in the range 73·6–83% were prepared by addition of water to oxonium perchlorate.

Oxidative properties as a function of acid concentration and temperature

Because of the non-reversibility of the reaction, the available oxidation potential of hot concentrated perchloric acid must be determined semi-quantitatively from the colour changes occurring in the oxidation of certain metal ions such as chromium, vanadium, cerium and manganese.

Procedure

A 20-ml portion of perchloric acid was placed in a 100-ml round-bottom flask fitted with a water-cooled condenser and teflon-mounted thermometer (Fig. 1). Then 30–40 mg of the reduced form of a suitable redox system were added as indicator. The reaction flask was mounted above a heating mantle (a modified Rogers ringburner[6] and wire gauze). The gas flow and the height of the flask were adjusted so that the temperature increased at a rate of about 1°/min, as shown in Fig. 2. The transition temperature indicated by the colour change of the redox couple was reproducible within 1°, the momentary pause in the temperature rise as the oxidation reaction occurred making this temperature easily discernible.

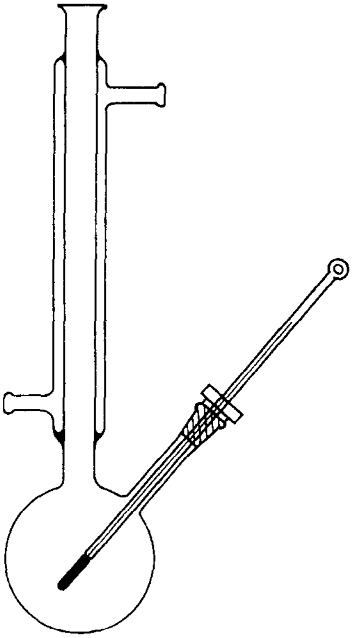

FIG. 1.—Oxidation test apparatus.

Oxidation of chromium. Chromium(III) is not oxidized to chromium(VI) by boiling perchloric acid of concentration below about 68%. It is oxidized by hot 70% perchloric acid and the chromium(VI) oxide formed is soluble in the hot acid but completely precipitated at room temperature. Chromium(III) perchlorate hexahydrate was used as indicator. The transition temperatures for various acid concentrations are shown in Fig. 3.

Oxidation of vanadium(IV). Vanadyl sulphate (40 mg) was used with 20-ml samples of the various acid strengths, the colour changes being from blue to green to orange upon heating, and the product was vanadic acid. The results are shown in Fig. 4.

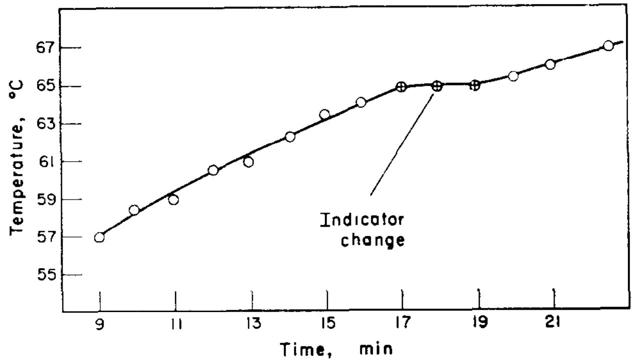

FIG. 2.—Typical temperature-time curve, showing temperature lag as reaction begins.

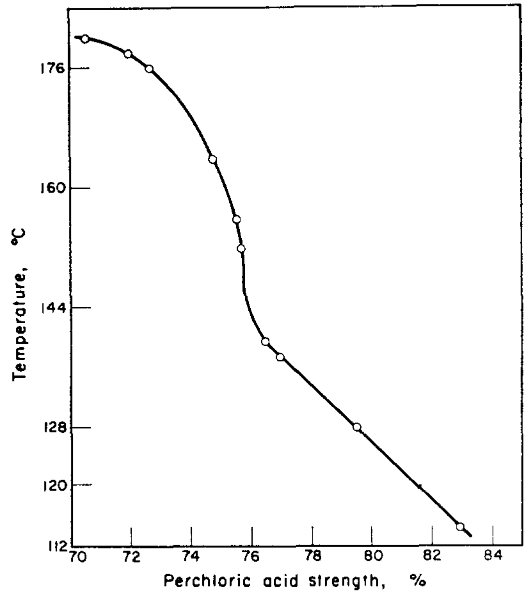

FIG. 3.—Oxidation of chromium(III).

Oxidation of cerium(III). The oxidation of cerium(III) perchlorate to perchloroatoceric acid by 72–80% perchloric acid is recorded in Fig. 5. The indicator colour change is from colourless to orange.

Oxidation of manganese. Manganese perchlorate is oxidized by 69–81% perchloric acid, presumably to manganese dioxide, as indicated by the appearance of a brown colour. The results obtained are shown in Fig. 6. On heating at higher temperatures the manganese is oxidized to yield a light purple product, probably permanganate.

DISCUSSION

Qualitative estimation of oxidation potentials

In the oxidation of chromium, vanadium, cerium and manganese, Figs. 3–6, a plateau occurs in the plots of oxidation temperature *vs.* acid concentration, in each case at approximately 76·5% perchloric acid concentration. The significance of this is not clear, though it may indicate a change of mechanism.

Much more important is the determination of the oxidation potentials provided.

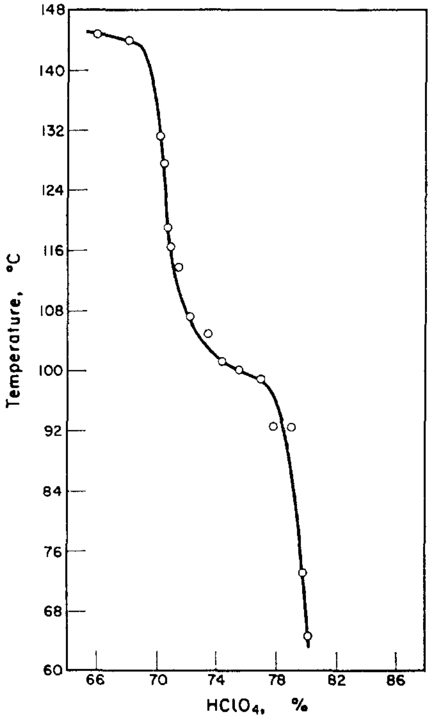

FIG. 4.—Oxidation of vanadium(IV).

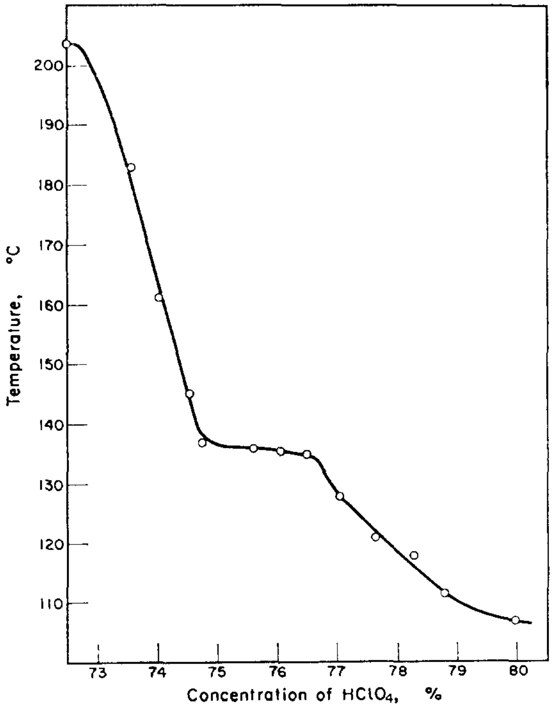

FIG. 5.—Oxidation of cerium(III).

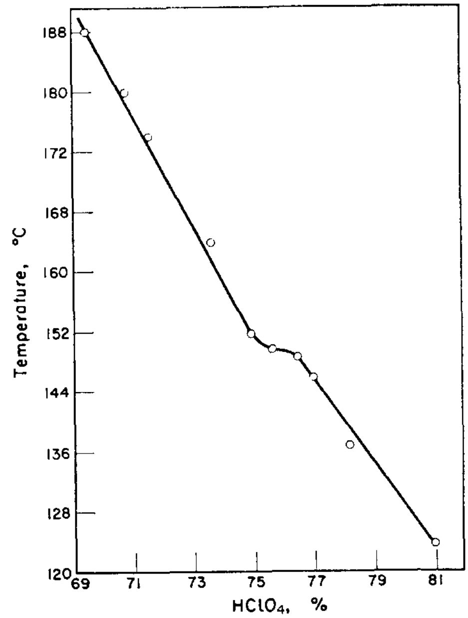

Fig. 6.—Oxidation of manganese(II).

The standard oxidation potential of the Ce(III)/Ce(IV) couple in 1F perchloric acid has been determined[7] by Smith and Goetz to be 1·70 V and increases to 1·88 V in 8F perchloric acid. Perchloric acid of 76·5% concentration is approximately 13·2F. Data for the oxidation potential of the Ce(III)/Ce(IV) couple[7] are plotted in Fig. 7. Assuming that these data can be extrapolated linearly to an acidity of 13·2F, an oxidation potential of 2·04 V is indicated for the 76·5% acid. These extrapolated values are not an underestimate of the real values if one accepts the common dictum that 80–100% concentration of perchloric acid inevitably causes explosion, a dictum which is reasonably justified for concentrations above 84·6%. From the extrapolated values of Fig. 7, the oxidation potential of 73·6% perchloric acid is comparable to that of ozone in acid solution and second only to that of fluorine in magnitude. Beyond doubt, acid more concentrated than the monohydrate, OH_3ClO_4, makes available oxidation potentials of at least 2·1 V.

Perchloric acid as oxygen donor in the destructive oxidation of organic material

From the data presented it must be concluded that perchloric acid provides a source of available oxygen, which can be controlled by variation of concentration and temperature.

In the wet oxidation of organic material by perchloric acid alone, a constant acid concentration[1] is obtained by performing the digestions under reflux with the Bethge apparatus. In destructive oxidation of organic matter by either "the liquid fire reaction"[8] or "the periodic acid liquid fire reaction",[9] the rate of oxidation is controlled by gradual elevation of the temperature under non-reflux conditions.

The Kjeldahl destruction of organic matter has been materially shortened by the dropwise addition of perchloric acid. A general scheme for this destructive oxidation by use of mixed sulphuric and perchloric acids has been described,[10] and a preliminary digestion with boiling concentrated sulphuric acid has also been followed by the more convenient addition of concentrated perchloric acid in bulk instead of dropwise.[11] The use of hot concentrated mixed sulphuric and perchloric acids raises the question of the equivalent perchloric acid concentration thus provided. This has been determined in the following manner. Reagent grade sulphuric acid (95·1 % H_2SO_4 by analysis) was mixed with 72 % perchloric acid over the range 5, 10, 15, 30 and 50 % v/v perchloric acid. The oxidation potentials of these mixtures were determined in the way already described, and used as a measure of the concentrations of perchloric acid that would be equivalent to these mixtures in oxidizing power. The results are shown in Fig. 8. For the mixtures used in the general procedures quoted,[10,11] the equivalent perchloric acid concentration is 78 %. Knecht[12] has recently used hot perchloric and sulphuric acid mixtures to oxidize cerium(III) and has concluded that the oxidation potential of the mixture is at least 2 V.

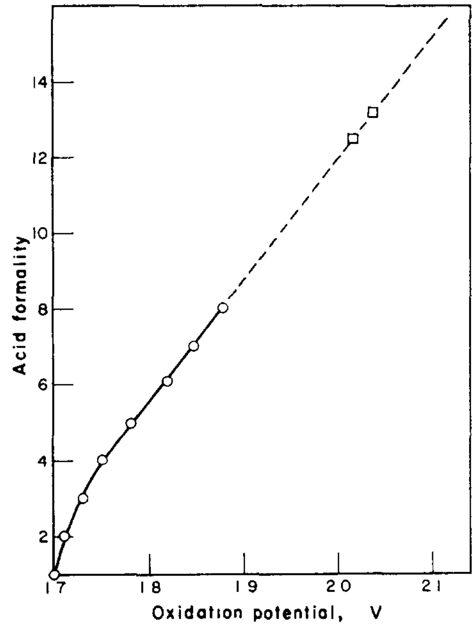

FIG. 7.—Redox potential of the Ce(III)/Ce(IV) couple as a function of perchloric acid concentration.

Applications of 80 % *perchloric acid*

Iodine has been oxidized in the vapour phase by subliming it into the fumes of 72·5 % perchloric acid at its boiling point. By its addition to 78–80 % perchloric acid and heating to temperatures lower than the boiling point, iodine is oxidized to iodic acid in the liquid phase.

Oxidation of sulphur to sulphate and oxides of sulphur by its addition to boiling 72·5 % perchloric acid is well known; flowers of sulphur can be oxidized at room temperature by addition to 78–80 % perchloric acid, this oxidation being highly exothermic.

Addition of sodium oxalate to boiling 72·5 % perchloric acid results in its oxidation

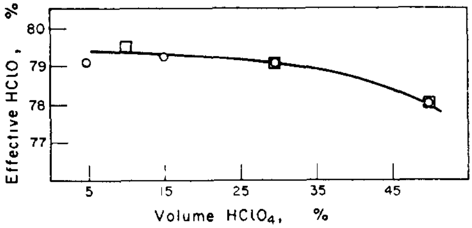

FIG. 8.—Perchloric acid concentration equivalent to a mixture of 95% perchloric acid and 95% sulphuric acid.

to carbon dioxide without violent reaction.[1] The addition of sodium oxalate to 78–80% perchloric acid followed by heating results in quiet oxidation to carbon dioxide. Vanadium acts as a catalyst.

Galena dissolves in 81% perchloric acid at 40–90° to give a colourless solution. The lead sulphate formed is soluble in this strength of perchloric acid and is precipitated on dilution with water. This reaction is also highly exothermic. Insufficient sulphate is produced to precipitate all the lead. Pyrrhotite (magnetic FeS) dissolves in 81% perchloric acid at 50° with notable vigour. This reaction is highly exothermic and partially converts the iron into anhydrous iron(III) sulphate, which is insoluble in the concentrated acid. Upon dilution with water and warming, a clear solution results which may be green because of the presence of nickel. Other sulphur ores were not tested since it is quite evident that by the use of 78–80% perchloric acid, effective oxidation of sulphur and dissolution of the ore can be obtained.

On heating with 77% perchloric acid, wool yarn gives a chocolate-brown solution which rapidly oxidizes quietly at the temperature of the boiling point of the acid, giving a yellow solution. The presence of unoxidized organic matter is indicated by the appearance of a green colour on addition of a few milligrams of chromium(III) perchlorate. Vanadyl sulphate (1 mg) can be added as catalyst. Ammonium perchlorate resulting from the protein conversion crystallizes out on cooling. Cellulose is not set on fire by 80% perchloric acid at room temperature.

Reduction products of 78–80% *perchloric acid*

In the oxidations described the reduction products were tested for presence of hydrochloric acid. Only very small amounts were found in the gaseous products or the acid residue. In the oxidation of cerium(III) the resultant perchloratoceric acid is unstable at 100–190° and reacts to evolve oxygen.

In none of the work described here was it deemed necessary to work with protection against possible violet reactions. The commercial availability of crystalline perchloric acid monohydrate, $HClO_4{\cdot}H_2O$, and its permissible distribution by common carrier should result in numerous practical applications of 73·6–84·6% perchloric acid.

Zusammenfassung—Die in Überchlorsäure im Konzentrationsbereich 70–80% vorliegenden Oxidationspotentiale wurden untersucht. Der Einfluß von Säurekonzentration und Temperatur auf die Oxidation von Chrom, Vanadium, Cer und Mangan wurde studiert. Die Oxidations-potentiale liegen anscheinend bei 2,0–2,1 V oder höher. Überchlorsäuremonohydrat $HClO_4{\cdot}H_2O$, das 84,6% Überchlorsäure enthält, ist im Handel zu erhalten und zum Transport auf den normalen Wegen zugelassen. Es kann zu Säurekonzentrationen von 73,6%

($HClO_4 \cdot 2H_2$ Oentsprechend) an aufwärts verdünnt werden. Gemische von Überchlorsäure und Schwefeläure entsprechen hochkonzentrierter Überchlorsäure und können zum Lösen von Erzen und zum Zerstören organischen Materials dienen.

Résumé—On a effectué une étude des potentiels d'oxydation probables apportés par l'acide perchlorique dans le domaine de concentration 70–80%. On a étudié l'influence de la concentration de l'acide et de la température sur l'oxydation du chrome, du vanadium, du cérium et du manganèse. Les potentiels d'oxydation valables paraissent être 2,0–2,1 V ou plus. Le monohydrate de l'acide perchlorique $HClO_4$, H_2O, contenant 84,6% d'acide perchlorique, est devenu commercialement accessible et sa répartition autorisée par transport ordinaire. On peut le diluer pour avoir des concentrations en acide allant de 73,6% (correspondant à $HClO_4 \cdot 2H_2O$) aux valeurs supérieures. L'acide perchlorique mélangé à l'acide sulfurique est équivalent à des concentrations élevées d'acide perchlorique et peut être utilisé pour la dissolution de minerais et la destruction de la matière organique.

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ISOLATION OF OSMIUM AND RUTHENIUM BY ION-EXCHANGE PAPER AND SUBSEQUENT DETERMINATION BY X-RAY FLUORESCENCE

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Summary—Quantitative separations of microgram quantities of osmium and ruthenium from large proportions of copper, iron and nickel were accomplished by the use of anion-exchange paper. Accurate determinations of osmium and ruthenium were made by adaptation of X-ray fluorescence. Wet methods for the dissolution of the paper and exchanger and subsequent wet determinations of osmium and ruthenium are discussed.

METHODS of separating both microgram and milligram amounts of the six platinum metals from large proportions of iron, copper and nickel by cation-exchange columns have been reported.[1] The isolation of rhodium, iridium, platinum and palladium by anion-exchange columns has also been the subject of a number of papers.[2] However, no method for the successful isolation of osmium or ruthenium on anion-exchangers has yet been recorded. By the application of anion-exchange paper the present authors hoped to avoid determinations of osmium and ruthenium involving treatment of large volumes of effluents. Furthermore, it seemed probable that use of an anion-exchange paper would permit subsequent determination by X-ray fluorescence. The successful accomplishment of both objectives is described below. The method of determination is rapid and accurate and the separation from base metals is complete for osmium, with only slight losses of ruthenium.

EXPERIMENTAL

Reagents

Ammonium chlororuthenate. Prepared by dissolving 1·7 g of the salt in 200 ml of water and 20 ml of concentrated hydrochloric acid, filtering twice and diluting to 1 l. with 2*N* hydrochloric acid. Precipitation by thionalide[3] indicated a ruthenium concentration of 0·4701 mg/ml. Working solutions were prepared by appropriate dilution to make 2*N* hydrochloric acid.

Ammonium chloro-osmate. Prepared by dissolving 2·3 g of the salt in 200 ml of water and 40 ml of concentrated hydrochloric acid. The solution was heated gently for 30 min and filtered through a sintered glass crucible; the filtrate was diluted to 1 l. Precipitation by thionalide[4] gave the osmium concentration as 0·851 mg/ml. Working solutions were adjusted to pH 1.

Base metal solutions. Prepared by dissolving 650 g of $FeCl_3.6H_2O$, 80 g of $NiCl_2.6H_2O$ and 50 g of $CuCl_2.2H_2O$ in 200 ml of concentrated hydrochloric acid and diluting to 2 l. The weight of base metal in 150 ml of this solution was equal to the total weight of an assay button. Solutions of single base metals were similarly prepared.

Apparatus

Ion-exchange papers. Disks 3·5 cm in diameter were prepared from Reeve Angel SB 2 anion-exchange paper.

X-Ray equipment. Philips X-ray generator, goniometer and electronic circuit panel.

Filtering equipment. This was a modification of that described by Campbell *et al.*[5] The filter paper was held in a fixed position on a narrow rim fused to the inside wall of a funnel. An open female joint, (34/35), fitted into the funnel with the smooth, evenly cut end fused to the inner wall of the funnel immediately adjacent to the rim and to the outer circumference of the rim. The disk of anion-exchanger was placed over the rim. The male joint was fitted into the female joint with the lower edge pressing tightly against the paper resting on the rim. The upper cup served as a funnel.

Determination of ruthenium

Procedure. Aliquots of the ruthenium solutions containing from 10–100 μg of ruthenium were evaporated to incipient dryness in the presence of 5 ml of 2% sodium chloride solution and several drops of concentrated hydrochloric acid. The residue was dissolved and diluted to 20–25 ml and the acidity was adjusted to pH 0·3. The ion-exchange paper disk was inserted into the filtering apparatus and several ml of hydrochloric acid, pH 0·3, were passed through the paper. The ruthenium solution was passed through the paper twice at a rate of 1 drop/sec and the paper was washed with 10–20 ml of hydrochloric acid at pH 0·3. After filtration, the disk was removed from the apparatus, pressed between two pieces of filter paper, and allowed to dry completely.

For the X-ray determination of ruthenium the $K_{\alpha 1}$ line was used because of its high intensity for ruthenium and lower interference as compared with the other lines. The X-ray tube was operated at 50 kV and 20 mA and the scintillation detector was operated at 800 kV. With a lithium fluoride crystal, the $K_{\alpha 1}$ line occurred at 18·37° (2θ).

The goniometer setting was not readjusted during the period of determination and the same mylar film on the bottom of the standard metal sample holder, supplied with the Philips X-ray fluorescence instrument, was used throughout a series of sample determinations. Pulse-height analysis was employed in every case.* The disks were placed in the sample holder which was positioned in the path of the X-rays. Ten readings were taken, with a fixed time of 10 sec. The opposite side of the disk was then exposed to the X-rays and a further ten readings were taken and the results averaged. A series consisted of one or two standards, a blank, and several samples. The blank was prepared in exactly the same manner as the samples. The metal content of the sample was calculated from the standard as follows.

$$(N_{ST} - N_B)/n = x$$

Weight of ruthenium (μg) in sample = $(N_S - N_B)/x$ where N_{ST} = counts/sec from the standard, N_S = counts/sec from the sample, N_B = counts/sec from the blank, n = μg of ruthenium on the standard disk, x = the counts per μg of ruthenium in 10 sec. As noted below, the background counts were consistent and it was found experimentally that the counts varied directly with the weight of ruthenium.

Alternative wet method of determination. The ion-exchange disk containing the ruthenium was placed in a distillation flask with a solution of 20 g of sodium hydroxide in 150 ml of water. The trap contained 10% potassium permanganate solution. The receiver solutions, which were chilled in ice-baths, consisted of hydrochloric acid (1 + 2) containing 3% of hydrogen peroxide. Chlorine was bubbled slowly through the pot liquid, and was absorbed immediately by the sodium hydroxide, forming sodium hypochlorite and hydrochloric acid. After approximately 20 min, the temperature rose quickly and a rapid effervescence occurred. If the conditions were not controlled carefully, froth rose in the flask and bubbled over into the trap. More control was achieved if the sodium hydroxide contained little carbonate and particularly if it was boiled and cooled before use. During the reaction, the paper disintegrated quickly and the finely divided particles of resin disappeared completely. After the reaction had ceased, the chlorine was allowed to bubble through the solution for approximately 10 min or until it was no longer absorbed.

The liquid in the pot was boiled for 30 min after the chlorine supply had been disconnected, and the trap was refluxed for 15 min. The receiver traps were then removed from the apparatus and the solutions were evaporated on a steam-bath to 10 ml. Three ml of 2% sodium chloride solution were added and the samples were evaporated to near dryness. The salt residue was dissolved in distilled water and hydrochloric acid and the ruthenium was determined colorimetrically with thiourea.[6] The readings were taken at 650 mμ, with matched 5-cm silica cells for less than 9 ppm, and 1-cm cells for 9–18 ppm.

The results for the X-ray determination of ruthenium and comparisons with wet methods are recorded in Tables I, II, III and V.

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* For ruthenium the window parameters were 22·5 V for the baseline and 16·8 V for the window. In the case of osmium, repair of the instrument during the determinations necessitated adjustments of the window dimensions and thus those dimensions used would be inapplicable to a machine in good working order.

Determination of osmium

Procedure. The sample preparation and X-ray determination used for osmium were similar to those used for ruthenium. In order to achieve quantitative retention of osmium on the anion-exchange paper, a prior evaporation to dryness was not recommended (see discussion). Aliquots of the stock solution containing from 17 to 85 μg of osmium were diluted to 25 ml. The acidity was adjusted to pH 1 before a single passage through the disk, which had been washed with hydrochloric acid at pH 1. The $L_{\alpha 1}$ line occurring at a goniometer setting of 40·40° (2θ) was used as it gave the highest intensity for osmium, compared to the background.

Alternative wet method. The osmium on the anion-exchange paper was destroyed by sodium hydroxide and chlorine in a distillation flask by a procedure similar to that used for ruthenium. The distillate was collected in receiving solutions containing 3% of hydrogen peroxide. The receiving solutions, kept in an ice-bath, were transferred to a second distillation flask and distilled with hydrogen peroxide as oxidant[7] was made. Osmium was determined in the distillate by addition of 3 ml of 10% thiourea solution. With freshly distilled solutions, the rose colour developed immediately and it was not necessary to add stannous chloride; low results were obtained unless the solution containing the freshly distilled osmium was allowed to stand overnight after the thiourea had been added. Allan and Beamish also found that overnight standing was advisable to obtain maximum colour for osmium concentrations of 5 μg/ml. Determinations were made at 480 mμ in matched 5-cm silica cells. The results for the determination of osmium and comparison with wet methods are recorded in Tables VI, VII and VIII.

Separation of osmium or ruthenium from base metals by anion-exchange

Initial experiments were made to determine that no iron, copper, or nickel would be retained on the anion-exchange paper. Separate solutions of iron, copper and nickel at pH 0·3 were filtered individually through anion-exchange paper. The disks were washed well with a hydrochloric acid solution at the same pH. Each disk was burned to a fine ash in a crucible. The ashes were dissolved and appropriate spot tests performed. No trace of iron, copper or nickel was found.

Then 10–100 μg of ruthenium were added to 10–20 ml of the mixed base metal solution which was then evaporated to incipient dryness. In order to avoid a brown turbidity the solution was evaporated to incipient dryness only and the residue was dissolved in a small amount of concentrated hydrochloric acid before dilution to 25 ml and pH 0·3. The green solution was filtered through an ion-exchange disk as previously described. The ruthenium retained on the disk was determined by X-ray fluorescence.

In the case of osmium the evaporation to dryness was omitted and the solution was used at pH 1. The results for the determination of osmium and ruthenium after separation from base metals are shown in Tables IX and X.

RESULTS AND DISCUSSION

TABLE I.—RECOVERY OF RUTHENIUM BY X-RAY AND WET METHODS

X-Ray, μg	Wet method, μg
17·8	17·7
36·0	34·1
18·8	18·4
8·8	9·2
18·5	17·8

The results given in Table I comparing the X-ray fluorescence method with the wet method for ruthenium show good precision. In the sample preparation, it was necessary to evaporate the solutions to incipient dryness in the presence of sodium chloride and hydrochloric acid. Initial experiments revealed that unless this evaporation was made, less than 80% of the ruthenium was retained on the anion-exchange disk. The retention was improved considerably by evaporation but slightly less than 100% of the ruthenium was retained on the disk. Chemical determinations on the effluent showed the presence of ruthenium and these losses are shown in Table II. The percentage of ruthenium passing through the disk was always small and reasonably consistent.

TABLE II.—RETENTION OF RUTHENIUM BY ANION-EXCHANGE PAPER

No.	Added, μg	Retained on disk, μg	Difference, μg	Loss, %
1	470·1	456·8	13·2	2·8
2	470·1	456·5	13·6	2·9
3	188·0	182·6	5·4	2·9
4	188·0	182·8	5·2	2·8
5	94·0	91·4	2·6	2·8
6	47·0	45·7	1·3	2·8
7	47·0	46·0	1	2·1
8	18·8	18·4	0·4	2·8
9	18·8	17·6	1·2	6·8

Excluding No. 9, average = 2·7

With the filtering apparatus used, the ruthenium was uniformly distributed over the ion-exchange paper. Uniform distribution was also achieved when the solution was passed through an anion-exchange disk held by gentle suction to the porous bottom of a filtering stick (3·5 cm diameter), but in this case up to 50% of the ruthenium passed through the disk. Attempts to improve the results by using various suction rates from 10 to 60 drops/min failed to improve the results and the use of suction was therefore discontinued.

The net count $N_S - N_B$ was used to determine the number of counts from the ruthenium alone. Fortunately, the blank was sufficiently precise to be used as a means of finding the background.

The only variation in the composition of the sample solutions aside from the concentrations of ruthenium and the very slight differences in acidity, was the amount of

TABLE III.—RUTHENIUM BY X-RAY FLUORESCENCE

Ruthenium on disk,* μg	Recovered, μg
91·5	91·6
91·5	91·5
73·2	73·2
54·9	55·2
45·7	45·9
45·7	46·3
36·6	36·5
36·6	36·1
36·6	36·0
36·6	36·3
18·3	18·0
18·3	17·8
18·3	18·8
18·3	18·5
9·2	8·8
9·2	10·5
9·2	9·7
9·2	9·5

sodium chloride present in the solution. Blanks were prepared with various amounts of 2% sodium chloride solution (2–15 ml). The results are summarized in Table IV and show no significant variations.

TABLE IV.—EFFECT OF SODIUM CHLORIDE ON BLANK

Blank count, *cps*	2% NaOH used in blank, *ml*
372·1	15
325·5	6
328·2	10
325·7	5

* Obtained by subtracting the 3% loss to effluent from the weight of added ruthenium.

Because of fluctuations in the machine from day to day, fresh standardizations had to be made each time a set of samples was determined. Two standards containing a known amount of ruthenium were prepared and the counts were read for each of the samples, the standards and the blank.

TABLE V.—RECOVERY OF RUTHENIUM FROM THE ANION-EXCHANGE PAPER BY DISTILLATION

In original solution, *μg*	In effluent, *μg*	Ru in receivers after distillation from paper, *μg*
470·1	13·5	456·2
470·1	13·2	456·0
94·0	negligible	91·6
47·0	negligible	46·0
940·4	28·1	901·9

The results tabulated in Table V show that the wet method removed all of the ruthenium from the resin and volatilized it completely. After the sample had been prepared, the X-ray determination required only 15 min as compared to 2 hr for the wet method.

TABLE VI.—DETERMINATION OF OSMIUM BY X-RAYS

Added *μg*	Found, *μg*
34·0	33·1
85·1	85·6
85·1	84·5
85·1	85·2
17·0	16·8
425·5	424·8
525·5	424·3
425·5	425·4

TABLE VII.—DETERMINATION OF OSMIUM BY DISTILLATION

In solution, μg	Recovered in distillate, μg
34·0	33·1
85·1	85·6
85·1	84·5
85·1	85·2
17·0	16·8
425·5	424·8
425·5	424·3
425·5	425·4

TABLE VIII.—DETERMINATION OF OSMIUM BY X-RAY AND WET METHODS

Added, μg	X-Rays, μg	Wet method, μg
34·0	33·5	33·2
34·0	33·8	33·0
17·0	16·5	16·3
85·1	85·0	84·9
85·1	84·8	84·4

Tables VI, VII and VIII show that the X-ray fluorescence method and the wet method for osmium were equally successful for the determination of osmium. In the case of osmium, there was no problem of incomplete retention on the anion-exchange disk. There was also no loss of osmium from volatilization when the osmium on the paper was struck with X-rays. Some loss had been expected because of the ease with which osmium tetroxide is volatilized.

It may be noted that while the accuracy of the X-ray determination for ruthenium is excellent, there is a constant 3% loss through the anion-exchange paper. While the constancy of this loss allows the use of a small correction factor, any improvement in the retention will reduce or eliminate the need for a factor. Table II indicates that the loss on 20 μg of ruthenium is about 1 μg and therefore of little significance in the colorimetric determination.

Tables IX and X illustrate the applicability of anion-exchange and X-ray determinations to the separation of microgram quantities of osmium and ruthenium from milligram of the base metals. Losses of osmium, presumably as the tetroxide, during evaporation of osmium solutions containing base metals were reported by Van Loon and Beamish.[9] The magnitude of the loss varied with the identity of the base metal, the highest losses occurring in the presence of iron, with significant losses in the case of copper and small losses in the presence of nickel. In an earlier paper, Van Loon and Beamish[10] found loss of osmium from boiled hydrochloric acid solution presumably containing only hexachloro-osmate. This was, of course, contrary to the long known stability of boiling distillates of the hexachloro-osmate obtained by distilling the tetroxide into hydrochloric acid. Fay[11] was unable to corroborate the findings of Van Loon and Beamish, reporting that no losses occurred from evaporation of hydrochloric acid solutions of hexachloro-osmate. The present authors made some effort to explain the contrary findings. It was confirmed that volatilization losses from

TABLE IX.—EFFECT OF BASE METALS IN ORIGINAL SOLUTIONS ON X-RAY DETERMINATION

Ruthenium in solution µg	Found, no base metal present µg	Found, 300 mg of base metal present in the orginal solution, µg
18·8	18·2	
18·8	18·0	
18·8	18·5	
18·8		18·2
18·8		18·5
18·8		18·9
37·5	36·1	
37·5	36·0	
37·5	36·3	
37·5		36·0
37·5		36·2
37·5		36·5
37·5		33·5
94·0	91·6	
94·0		90·2

TABLE X.—DETERMINATION OF OSMIUM BY X-RAYS AFTER SEPARATING FROM 300 mg OF BASE METALS

Taken, µg	Found, µg
34·0	33·7
34·0	34·4
68·1	68·2
68·1	67·9
85·1	84·7
17·0	18·1
17·0	16·6

hexachloro-osmate did occur but only in the presence of oxides of nitrogen in the atmosphere or in the presence of certain base metal or oxidizing impurities in the hydrochloric acid used. Evaporations in fume chambers free from oxides of nitrogen or dust containing iron were not accompanied by osmium losses. These findings resulted in the above procedure for osmium being slightly modified from that recommended for ruthenium, in which evaporations to dryness were made.

Zusammenfassung—Mit Ionenaustauschpapier wurden Mikrogrammengen Osmium und Ruthenium quantitativ von froßen Mengen Kupfer, Eisen und Nickel abgetrennt. Osmium und Ruthenium wurden durch Röntgenfluoreszenz genau bestimmt. Naßverfahren zur Auflösung von Papier und Austauscher sowie nachfolgende Naßbestimmungen von Osmium und Ruthenium werden diskutiert.

Résumé—On a réalisé des séparations quantitatives de quantités de l'ordre du microgramme d'osmium et de ruthénium de grandes proportions de cuivre, fer et nickel par l'emploi de papier échangeur d'anions. Des déterminations précises d'osmium et de ruthénium ont été faites par adaptation de la fluorescence aux rayons X. On discute de méthodes par voie humide pour la dissolution du papier et de l'échangeur et de dosages subséquents par voie humide de l'osmium et du ruthénium.

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METAL CHELATE EXCHANGE IN THE ORGANIC PHASE—II

EXTRACTION AND EXCHANGE CONSTANTS OF DITHIZONATES AND DIETHYLDITHIOCARBAMATES

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Summary—Dithizonates and diethyldithiocarbamates of Ag, Tl(I), Cu(II), Zn, Cd, Hg(II), Pb, Fe(II), Co(II), Ni, Pd(II), In(III), As(III), Sb(III), Bi, Se(IV) and Te(IV) have been prepared and their reactions in carbon tetrachloride have been studied spectrophotometrically. From the exchange constants determined, the extraction constants of metal diethyldithiocarbamates have been calculated. Where formation of mixed chelates has been observed, corresponding exchange constants have been determined. Finally, the influence of organic solvents (CCl_4, $CHCl_3$, C_6H_6 and C_6H_5Cl) on the exchange reaction of zinc diethyldithiocarbamate with dithizone has been investigated.

IN OUR previous paper,[1] metal chelate exchange in the organic phase has been described and its theory given. It was shown that the equilibrium constant E of any exchange reaction is related to the extraction constants K of the metal chelates involved. Thus from known K-values, the exchange constant E can be calculated and the course of the exchange reaction predicted. Alternatively, by measurement of the exchange constant, the extraction constant of one metal chelate can be calculated when the extraction constant of the second chelate is known. The latter approach has been chosen to determine metal diethyldithiocarbamate extraction constants, which are very high and thus difficult to determine by the conventional methods. Dithizone has been used as the second chelating agent because metal dithizonates (and dithizone itself) are coloured and their extraction constants are well known.

During our investigation an experimental methodology has been developed which enables one to obtain reliable results with minimum effort.

THEORETICAL

Investigation of mixed chelates

From the theory given in the previous paper,[1] it follows that the equilibrium constant of the exchange reaction between metal dithizonate $M(HDz)_N$ and diethyldithiocarbamic acid HDDC [or alternatively between metal diethyldithiocarbamate $M(DDC)_N$ and dithizone H_2Dz] in the organic phase can be expressed as

$$E_{M(HDz)_N-HDDC} = \frac{[M(DDC)_N][H_2Dz]^N}{[M(HDz)_N][HDDC]^N} = \frac{K_{M(DDC)_N}}{K_{M(HDz)_N}} \tag{1}$$

where $K_{M(DDC)_N}$ and $K_{M(HDz)_N}$ are the extraction constants of metal diethyldithiocarbamate and dithizonate respectively, and subscripts indicating the phase are omitted for simplicity.

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However, when mixed chelates are formed the exchange reactions are more complicated. Thus, the reaction of copper dithizonate with diethyldithiocarbamic acid can be described by the reactions

$$\mathrm{Cu(HDz)_2 + HDDC = Cu(HDz)(DDC) + H_2Dz} \tag{2}$$

$$\mathrm{Cu(HDz)(DDC) + HDDC = Cu(DDC)_2 + H_2Dz} \tag{3}$$

with equilibrium constants

$$E'_{\mathrm{Cu(HDz)_2-HDDC}} = \frac{[\mathrm{Cu(HDz)(DDC)}][\mathrm{H_2Dz}]}{[\mathrm{Cu(HDz)_2}][\mathrm{HDDC}]} \tag{4}$$

and

$$E''_{\mathrm{Cu(HDz)(DDC)-HDDC}} = \frac{[\mathrm{Cu(DDC)_2}][\mathrm{H_2Dz}]}{[\mathrm{Cu(HDz)(DDC)}][\mathrm{HDDC}]} \tag{5}$$

From equations (4) and (5) it follows that

$$(E'_{\mathrm{Cu(HDz)_2-HDDC}})(E''_{\mathrm{Cu(HDz)(DDC)-HDDC}}) = \frac{[\mathrm{Cu(DDC)_2)}][\mathrm{H_2Dz}]^2}{[\mathrm{Cu(HDz)_2}][\mathrm{HDDC}]^2}$$

$$= \frac{K_{\mathrm{Cu(DDC)_2}}}{K_{\mathrm{Cu(HDz)_2}}} = E_{\mathrm{Cu(HDz)_2-HDDC}}\,. \tag{6}$$

The formation of a mixed chelate can be investigated by measuring the spectrum of the mixture of diethyldithiocarbamate and dithizonate of the same metal. For example, in the case of copper the formation of a mixed chelate Cu(HDz)(DDC) occurs according to the reaction

$$\mathrm{Cu(DDC)_2 + Cu(HDz)_2 = 2Cu(HDz)(DDC)} \tag{7}$$

with equilibrium constant

$$E_{\mathrm{Cu(DDC)_2-Cu(HDz)_2}} = \frac{[\mathrm{Cu(HDz)(DDC)}]^2}{[\mathrm{Cu(DDC)_2}][\mathrm{Cu(HDz)_2}]} = \frac{E'_{\mathrm{Cu(HDz)_2-HDDC}}}{E''_{\mathrm{Cu(HDz)(DDC)-HDDC}}}\,. \tag{8}$$

Influence of organic solvent

The extraction constant of a metal chelate $\mathrm{MA_N}$ can in general be expressed as follows[2]

$$K_{\mathrm{MA_N}} = \frac{P_{\mathrm{MA_N}}\beta_{\mathrm{MA_N}}K_{\mathrm{HA}}^{N}}{P_{\mathrm{HA}}^{N}} \tag{9}$$

where $P_{\mathrm{MA_N}}$ and p_{HA} are the distribution coefficients of metal chelate $\mathrm{MA_N}$ and organic reagent HA respectively, $\beta_{\mathrm{MA_N}}$ is the overall stability constant of chelate $\mathrm{MA_N}$ and K_{HA} is the dissociation constant of the reagent HA. According to equation (1) the exchange constant is given by

$$\begin{aligned}\log E_{\mathrm{M(HDz)_N-HDDC}} &= \log K_{\mathrm{M(DDC)_N}} - \log K_{\mathrm{M(HDz)_N}}\\ &= \log P_{\mathrm{M(DDC)_N}} - \log P_{\mathrm{M(HDz)_N}} + \log \beta_{\mathrm{M(DDC)_N}}\\ &\quad - \log \beta_{\mathrm{M(HDz)_N}} + N \log K_{\mathrm{HDDC}} - N \log K_{\mathrm{H_2Dz}} + N \log P_{\mathrm{H_2Dz}}\\ &\quad - N \log P_{\mathrm{HDDC}}.\end{aligned} \tag{10}$$

When the organic solvent immiscible with water is changed, the stability constant of the metal chelate and the dissociation constant of the organic reagent remain constant. For this reason the ratio of exchange constants (E, E^*) in two different solvents is given by

$$\log E_{\mathrm{M(HDz)_N-HDDC}} - \log E^*_{\mathrm{M(HDz)_N-HDDC}} = \log \frac{P_{\mathrm{M(DDC)_N}}}{P^*_{\mathrm{M(DDC)_N}}} - N \log \frac{P_{\mathrm{HDDC}}}{P^*_{\mathrm{HDDC}}} - \log \frac{P_{\mathrm{M(HDz)_N}}}{P^*_{\mathrm{M(HDz)_N}}} + N \log \frac{p_{\mathrm{H_2Dz}}}{p^*_{\mathrm{H_2Dz}}}. \tag{11}$$

Because the ratio of the distribution coefficients of a metal chelate in two different solvents is approximately equal to the ratio of its solubilities $S_{\mathrm{MA_N}}$ and $S^*_{\mathrm{MA_N}}$ in these solvents,[2] *i.e.*,

$$\frac{P_{\mathrm{M(DDC)_N}}}{P^*_{\mathrm{M(DDC)_N}}} = \frac{S_{\mathrm{M(DDC)_N}}}{S^*_{\mathrm{M(DDC)_N}}} \quad \text{and} \quad \frac{P_{\mathrm{M(HDz)_N}}}{P^*_{\mathrm{M(HDz)_N}}} = \frac{S_{\mathrm{M(HDz)_N}}}{S^*_{\mathrm{M(HDz)_N}}} \tag{12}$$

it is possible to calculate the value of the exchange constant in various solvents if the solubility of metal chelate and the distribution coefficient of the corresponding organic reagent in these solvents are known.

EXPERIMENTAL

Reagents

Unless otherwise stated, all reagents were of analytical grade.

Organic solvents (carbon tetrachloride, chloroform, benzene and chlorobenzene). Twice distilled, and after the second distillation stored not longer than one day.

Dithizone (H_2Dz). Purified by solvent extraction in the usual way.[1,2]

Diethyldithiocarbamic acid (HDDC). Prepared as described in the previous paper.[1]

Metal dithizonates. Solutions of metal dithizonates in carbon tetrachloride, which do not contain any free dithizone, were prepared in substoichiometric conditions[3] by using an excess of metal relative to dithizone. The concentration of metal dithizonate could be calculated either from the amount of dithizone originally used or from the known value of the molar absorptivity of the chelate.[3,4] In this way solutions of the dithizonates of thallium, cadmium, mercury, cobalt, nickel, palladium and bismuth were prepared. Dithizonates of copper, iron(II) and mercury were obtained by extraction with an excess of dithizone; the unreacted dithizone was removed by shaking with dilute ammonia. In the case of iron(II) the concentration could not be determined because of the ready decomposition of the chelate.

Selenium(IV) dithizonate was prepared by successive extraction with an excess of dithizone in carbon tetrachloride from selenium(IV) solution in 5*M* hydrochloric acid. The dithizone remaining was removed by shaking with dilute ammonia. Selenium(IV) dithizonate in the organic extract was quantitatively transformed into diethyldithiocarbamate by addition of an excess of diethyldithiocarbamic acid in carbon tetrachloride. The amount of dithizone liberated in this reaction was determined spectrophotometrically at 620 mμ. From the results obtained in two experiments, it is quite evident that selenium is extracted from 5*M* hydrochloric acid as $Se(HDz)_4$; the ratio $H_2Dz:Se$ determined is between 3·9 and 4·2.

Tellurium(IV) is only partially extracted with dithizone. Because tellurium dithizonate is quickly destroyed by shaking with ammonia the composition of this chelate could not be determined.†

Metal diethyldithiocarbamates. Prepared similarly to the metal dithizonates. The concentration of metal diethyldithiocarbamate was determined spectrophotometrically at 436 mμ after conversion into copper diethyldithiocarbamate by treating with an excess of copper sulphate solution. Diethyldithiocarbamates of silver, mercury and palladium can be transformed into the copper chelate only in the presence of potassium iodide as masking agent.

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† After submission of this paper for publication a work by K. Marhenke and E. B. Sandell (*Anal. Chim. Acta*, 1967, **38**, 421) appeared in which formation of $Te(HDz)_2$ was reported, but these authors used a maximum acid concentration of 1*N* whereas we used 5*N* acid.

Solubility determination. Zinc dithizonate was precipitated by adding dithizone solution in dilute ammonia to a solution of zinc sulphate and sodium tartrate, filtered off, and dried in a desiccator over calcium chloride. A saturated solution of this chelate in carbon tetrachloride and the other organic solvents used was accurately diluted and its concentration determined spectrophotometrically. The solubility of zinc diethyldithiocarbamate in organic solvents was determined spectrophotometrically *via* copper diethyldithiocarbamate (see above).

Table I.—Determination of equilibrium constant $E_{\mathrm{Cu(DDC)_2-Cu(HDz)_2}}$.

Log of original concentrations		Log of equilibrium concentrations			Log $E_{\mathrm{Cu(DDC)_2-Cu(HDz)_2}}$
[Cu(DDC)$_2$]	[Cu(HDz)$_2$]	[Cu(DDC)$_2$]	[Cu(HDz)$_2$]	[Cu(HDz)(DDC)]	
−4·00	−5·10	−4·03	−5·82	−4·85	0·15
−4·00	−4·98	−4·04	−5·80	−4·80	0·25
−4·00	−4·88	−4·05	−5·63	−4·68	0·32
−4·00	−4·77	−4·05	−5·58	−4·61	0·41
−4·00	−4·72	−4·07	−5·48	−4·54	0·47
−4·00	−4·68	−4·08	−5·34	−4·48	0·46
−4·60	−4·98	−4·73	−5·42	−4·84	0·47
−4·30	−4·98	−4·42	−5·52	−4·70	0·44
−4·12	−4·98	−4·26	−5·55	−4·73	0·35
−3·90	−4·98	−3·97	−5·53	−4·65	0·20
					Average = 0·36 ± 0·05*

* The error quoted is the standard error of the mean.

Procedure

The experimental work and calculations of exchange constants were generally done as described before,[1] but for the more complicated calculations a computer was used. In most systems studied the exchange reaction in the organic phase took place very rapidly, but the exchange reactions of cobalt and nickel chelates are very slow (some hours or days).

RESULTS AND DISCUSSION

Thallium

To determine the exchange constant $E_{\mathrm{TlHDz-HDDC}}$ known amounts of thallium(I) diethyldithiocarbamate in carbon tetrachloride were mixed with known amounts of dithizone in the same solvent. The equilibrium concentrations of thallium(I) dithizonate and dithizone were determined by the mixed colour method. The equilibrium concentration of diethyldithiocarbamic acid is equal to the equilibrium concentration of thallium(I) dithizonate, and the equilibrium concentration of thallium(I) diethyldithiocarbamate is given by the difference between the original concentration of this species and the concentration of thallium(I) dithizonate formed.[1]

The mean value of the exchange constant log $E_{\mathrm{TlHDz-HDDC}}$ calculated from equation (1) is 3·53 ± 0·05. The extraction constant[2,4] of thallium(I) dithizonate is $\log K_{\mathrm{TlHDz}} = -3{\cdot}5$, thus the extraction constant of thallium(I) diethyldithiocarbamate is $\log K_{\mathrm{TlDDC}} = 3{\cdot}53 - 3{\cdot}5 = 0{\cdot}03$. The value of $\log K_{\mathrm{TlDDC}}$ determined by the solvent extraction method[5] is −0·53.

Copper

The absorption spectrum of the mixture of copper dithizonate and copper diethyldithiocarbamate (Fig. 1, curve 3) substantially differs from the spectrum of copper diethyldithiocarbamate (curve 1) and copper dithizonate (curve 2), which can be explained by the formation of a mixed chelate Cu(HDz)(DDC). Because attempts to separate the mixed complex were unsuccessful the determination of the equilibrium concentrations of all the species involved was carried out by computer from the spectra obtained. The mean value of $\log E_{\mathrm{Cu(DDC)_2-Cu(HDz)_2}}$ calculated from equation (8) is 0·36 ± 0·05 (Table 1).

From absorption spectra obtained during titration of copper dithizonate with diethyldithiocarbamic acid, it follows that the mixed chelate is formed first and is then further transformed into copper diethyldithiocarbamate [see equations (2) and (3)]. The equilibrium constant obtained, $\log E_{\mathrm{Cu(DDC)_2-Cu(HDz)_2}}$ = 0·4 ± 0·1, is in very good agreement with the value above. The precision of the measurements did not allow determination of the equilibrium concentration of diethyldithiocarbamic acid and for this reason the reaction between copper diethyldithiocarbamate and dithizone was studied. The mean value of $\log E''_{\mathrm{Cu(HDz)(DDC)-HDDC}}$ calculated from these experiments according to equation (5) is 2·1 ± 0·1. The value of $\log E'_{\mathrm{Cu(HDz)_2-HDDC}}$ is 2·1 + 0·4 = 2·5 [see equation (8)].

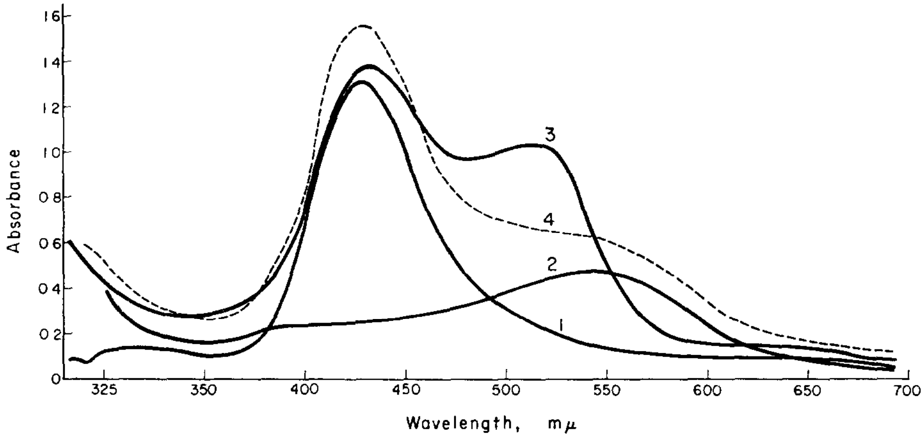

Fig. 1.—Absorption spectra of copper diethyldithiocarbamate ($10^{-4}M$)—curve 1, copper dithizonate ($10^{-5}M$)—curve 2, mixture of copper diethyldithiocarbamate ($10^{-4}M$) and copper dithizonate ($10^{-5}M$)—curve 3. (Curve 4—absorption spectrum of the mixture when mixed chelate is not formed.)

The total exchange constant is $\log E_{\mathrm{Cu(HDz)_2-HDDC}}$ = 2·1 + 2·5 = 4·6 [equation (6)]. The extraction constant of copper dithizonate[2,4] is $\log K_{\mathrm{Cu(HDz)_2}}$ = 9·5, so the extraction constant of copper diethyldithiocarbamate is $\log K_{\mathrm{Cu(DDC)_2}}$ = 4·6 + 9·5 = 14·1, which is in agreement with the value 13·7 determined by the solvent extraction method.[5] Typical results are shown in Table I.

Cadmium

From the investigation of the exchange reactions between cadmium diethyldithiocarbamate and dithizone or cadmium dithizonate and diethyldithiocarbamic acid the equilibrium constant $\log E_{\mathrm{Cd(HDz)_2-HDDC}}$ = 3·53 was determined. The extraction constant of cadmium diethyldithiocarbamate, $\log K_{\mathrm{Cd(DDC)_2}}$ = 3·53 + 1·6 = 5·13 (since[2,4] $\log K_{\mathrm{Cd(HDz)_2}}$ = 1·6), agrees with the value 5·41 determined by solvent extraction.[5]

Mercury

The exchange constant for mercury, $\log E_{\mathrm{Hg(HDz)_2-HDDC}} = 2{\cdot}31 \pm 0{\cdot}05$ was determined in a similar manner to that for cadmium. The extraction constant of mercury diethyldithiocarbamate, $\log K_{\mathrm{Hg(DDC)_2}} = 2{\cdot}31 + 26{\cdot}79 = 29{\cdot}1$ ($\log K_{\mathrm{Hg(HDz)_2}} = 26{\cdot}79$),[4] is very high. The solvent extraction values of $\log K_{\mathrm{Hg(DDC)_2}}$ are even higher (31·9–32·3).

Lead

When lead dithizonate is mixed with lead diethyldithiocarbamate, formation of a mixed chelate occurs only to a small extent. The exchange constant was determined as $\log E_{\mathrm{Pb(HDz)_2-HDDC}} = 4{\cdot}98 \pm 0{\cdot}05$, from which the extraction constant $\log K_{\mathrm{Pb(DDC)_2}} = 4{\cdot}98 + 0{\cdot}76 = 5{\cdot}74$ was obtained ($\log K_{\mathrm{Pb(HDz)_2}} = 0{\cdot}76$).[2,4] The value of the extraction constant, $\log K_{\mathrm{Pb(DDC)_2}} = 7{\cdot}77$, determined by the solvent extraction method,[5] is substantially higher.

Iron(II)

When iron(II) dithizonate was mixed with iron(II) diethyldithiocarbamate, formation of a mixed complex was observed. Because the dithizonate of iron(II) is rather unstable it was not possible to determine the corresponding exchange constants.

Cobalt(II)

Cobalt(II) dithizonate reacts with diethyldithiocarbamic acid very slowly. Only a great excess of reagent converts dithizonate completely into diethyldithiocarbamate. Cobalt diethyldithiocarbamate does not react with dithizone or the dithizonates of lead, zinc, *etc.* Cobalt(II) diethyldithiocarbamate appears to be oxidized in the organic phase to the very stable cobalt(III) chelate.

Nickel

From the absorption spectrum of a mixture of nickel dithizonate and nickel diethyldithiocarbamate it is evident that a mixed chelate Ni(HDz)(DDC) is formed. Because this chelate is thermodynamically rather stable and kinetically inert [the rate of reaching equilibrium is very slow (10–48 hr)] it was not possible to determine the exchange constant.

Palladium

From the absorption spectra of a mixture of palladium dithizonate and diethyldithiocarbamic acid or palladium diethyldithiocarbamate and dithizone the equilibrium concentrations of all species involved were determined by computer from their molar absorptivities. The exchange constant $\log E_{\mathrm{Pd(HDz)_2-HDDC}}$ calculated is $1{\cdot}6 \pm 0{\cdot}2$. Because the extraction constant of palladium dithizonate is higher than that of mercury dithizonate it can be expected that $\log K_{\mathrm{Pd(DDC)_2}} > 29$.

Indium

From the value of the exchange constant $\log E_{\mathrm{In(HDz)_3-HDDC}} = 4{\cdot}75 \pm 0{\cdot}10$, the extraction constant $\log K_{\mathrm{In(DDC)_3}} = 4{\cdot}75 + 4{\cdot}84 = 9{\cdot}59$ was calculated ($\log K_{\mathrm{In(HDz)_3}} = 4{\cdot}84$).[4]

Antimony

From the analysis of absorption spectra of a mixture of antimony(III) diethyldithiocarbamate and dithizone it was concluded that a mixed chelate $\mathrm{Sb(HDz)(DDC)_2}$ is formed (it is interesting to note that in similar conditions arsenic[1] forms a chelate AsDzDDC). The absorbance maximum of this chelate appears to be at 430 mμ, with molar absorptivity about 23×10^3.

The value of the exchange constant

$$\log E_{\mathrm{Sb(DDC)_3-H_2Dz}} = [\mathrm{Sb(HDz)(DDC)_2}][\mathrm{HDDC}]/[\mathrm{Sb(DDC)_3}][\mathrm{H_2Dz}]$$

is $-2{\cdot}47 \pm 0{\cdot}07$ (Table II). This value was verified by investigation of the exchange reaction

$$\mathrm{2Sb(DDC)_3 + Cd(HDz)_2 = 2Sb(HDz)(DDC)_2 + Cd(DDC)_2}.$$

The equilibrium constant of this reaction, $\log E_{\mathrm{Sb(DDC)_3-Cd(HDz)_2}} = -0{\cdot}91 \pm 0{\cdot}10$, so $\log E_{\mathrm{Sb(DDC)_3-H_2Dz}} = \frac{1}{2}(\log E_{\mathrm{Sb(DDC)_3-Cd(HDz)_2}} - \log E_{\mathrm{Cd(HDz)_2-HDDC}}) = \frac{1}{2}(-0{\cdot}91 - 3{\cdot}53) = -2{\cdot}22$.

Bismuth

From the value of the exchange constant $\log E_{\mathrm{Bi(HDz)_3-HDDC}} = 5{\cdot}72 \pm 0{\cdot}08$, the extraction constant of bismuth diethyldithiocarbamate, $\log K_{\mathrm{Bi(DDC)_3}} = 5{\cdot}72 + 10{\cdot}76 = 16{\cdot}48$, was determined ($\log K_{\mathrm{Bi(HDz)_3}} = 10{\cdot}76$).[2,4] This value agrees with the value 16·79 determined by the solvent extraction method.[5]

Selenium

The extraction constant of selenium(IV) diethyldithiocarbamate is much higher than that of selenium(IV) dithizonate and for this reason the investigation of the reaction between selenium(IV) diethyldithiocarbamate and dithizone [or between selenium(IV) dithizonate and diethyldithiocarbamic acid] did not give reproducible results. However, from the equilibrium constant, $\log E_{\mathrm{Se(HDz)_4-Cd(HDz)_2}} = -0{\cdot}78 \pm 0{\cdot}10$, of the exchange reaction

$$\mathrm{Se(HDz)_4 + 2Cd(DDC)_2 = Se(DDC)_4 + 2Cd(HDz)_2}$$

it is possible to calculate the value $\log E_{\mathrm{Se(HDz)_4-HDDC}} = 2 \log E_{\mathrm{Cd(HDz)_2-HDDC}} + \log E_{\mathrm{Se(HDz)_4-Cd(HDz)_2}} = 2 \times 3{\cdot}53 - 0{\cdot}78 = 6{\cdot}27$.

The result obtained was verified by investigation of the reaction

$$\mathrm{Se(HDz)_4 + 2As(DDC)_3 = 2AsDzDDC + Se(DDC)_4 + 2H_2Dz}$$

The equilibrium constant of this reaction is $\log E_{\mathrm{Se(HDz)_4-As(DDC)_3}} = -9{\cdot}2 \pm 0{\cdot}2$ from which $\log E_{\mathrm{Se(HDz)_4-HDDC}} = 2 \log E_{\mathrm{As(DDC)_3-H_2Dz}} + \log E_{\mathrm{Se(HDz.}_4\mathrm{-As(DDC)_3}} = 2 \times 7{\cdot}93 - 9{\cdot}2 = 6{\cdot}67$. The composition of $\mathrm{Se(HDz)_4}$ was established from the dithizone consumed in formation of the complex (16·2 and 16·8 μmole for 4·0 μmole of selenium) and the amount liberated (15·6 and 17·0 μmole per 4·0 μmole of selenium) in a reversion reaction.

Tellurium

The exchange constant $\log E_{\mathrm{Te(HDz)_4-HDDC}} \sim 5{\cdot}5$ was determined in a similar manner as the analogous constant for tellurium, assuming that $\mathrm{Te(HDz)_4}$ was the species concerned.

TABLE II.—Determination of equilibrium constant $E_{Sb(DDC)_3-H_2Dz}$

Log of original concentrations				Log of equilibrium concentrations				
[Sb(DDC)$_3$]	[H$_2$Dz]	[Sb(DDC)$_2$(HDz)]	[HDDC]	[Sb(DDC)$_3$]	[H$_2$Dz]	[Sb(DDC)$_2$(HDz)]	[HDDC]	log $E_{Sb(DDC)_3-H_2Dz}$
−3·04	−4·64			−3·05	−4·50	−4·88	−4·88	−2·21
−3·28	−4·61			−3·29	−4·75	−5·18	−5·18	−2·32
−3·34	−4·35			−3·35	−4·44	−5·08	−5·08	−2·37
−3·40	−4·61			−3·41	−4·72	−5·28	−5·28	−2·43
−3·58	−4·61			−3·59	−4·68	−5·42	−5·42	−2·57
−3·63	−4·35			−3·65	−4·39	−5·42	−5·42	−2·79
−3·88	−4·61			−3·89	−4·67	−5,46	−5·46	−2·36
		−4·23	−5·41	−4·44	−4·44	−4·98	−6·60	−2·70
							Average =	−2·47 ± 0·07*

* The error quoted is the standard error of the mean.

Influence of organic solvents

To investigate the influence of organic solvents on the exchange constant the reaction between zinc diethyldithiocarbamate and dithizone in various solvents was investigated. For carbon tetrachloride, chloroform, beznene and chlorobenzene the values of $\log E_{Zn(HDz)_2-HDDC}$ obtained were $0·24 \pm 0·03$, $1·10 \pm 0·05$, $0·30 \pm 0.05$ and $-0·36 \pm 0·10$ respectively.

From known values of the distribution coefficient of diethyldithiocarbamic acid[2,6] ($P_{HDDC} = 2350$ and 240 for chloroform and carbon tetrachloride respectively) and dithizone[2,7] ($P_{H_2Dz} = 6 \times 10^5$ and $1·5 \times 10^4$ for chloroform and carbon tetrachloride respectively) and from the solubility of zinc diethyldithiocarbamate ($S_{Zn(DDC)_2} = 0·39M$ in chloroform and $0·0405M$ in carbon tetrachloride) and zinc dithizonate ($S_{Zn(HDz)_2} = 0·061M$ in chloroform and $0·0072M$ in carbon tetrachloride) determined in the present work, it is possible to determine the difference [see equations (11) and (12)]:

$$\log E^{CHCl_3}_{Zn(HDz)_2-HDDC} - \log E^{CCl_4}_{Zn(HDz)_2-HDDC} = 1·27$$

Because of the low precision in determination of the P_{H_2Dz} values the experimentally determined difference (0·86) can be considered to be in agreement with that calculated theoretically.

CONCLUSION

The values of the equilibrium constants of exchange reactions in carbon tetrachloride investigated are summarized in Table III. In the case of copper, iron(II), nickel, arsenic(III) and antimony(III) the formation of mixed chelates was observed. The extraction constants of metal diethyldithiocarbamates, calculated from exchange

TABLE III.—Equilibrium constants of exchange reactions, *E*, and extraction constants of metal dithizonates, $K_{M(HDz)_N}$, and of diethyldithiocarbamates, $K_{M(DDC)_N}$

Reaction	log *E**	$\log K_{M(HDz)_N}$	$\log K_{M(DDC)_N}$
$AgHDz + HDDC = AgDDC + H_2Dz$	2·58 ± 0·03[1]	8·94[2]	11·52 (11·90)[5]
$TlHDz + HDDC = TlDDC + H_2Dz$	3·53 ± 0·05	−3·5[2]	0·03 (−0·53)[5]
$Cu(HDz)_2 + HDDC = Cu(HDz)(DDC) + H_2Dz$	2·5 ± 0·1		
$Cu(HDz)(DDC) + HDDC = Cu(DDC)_2 + H_2Dz$	2·1 ± 0·1		
$Cu(HDz)_2 + 2HDDC = Cu(DDC)_2 + 2H_2Dz$	4·6 ± 0·2	9·5[2]	14·1 (13·7)[5]
$Cu(HDz)_2 + 2Cu(DDC)_2 = 2Cu(HDz)(DDC)$	0·35 ± 0·05		
$Zn(HDz)_2 + 2HDDC = Zn(DDC)_2 + 2H_2Dz$	0·24 ± 0·03[1]	2·3[2]	2·54 (2·96)[5]
$Cd(HDz)_2 + 2HDDC = Cd(DDC)_2 + 2H_2Dz$	3·53 ± 0·05	1·6[2]	5·13 (5·41)[5]
$Hg(HDz)_2 + 2HDDC = Hg(DDC)_2 + 2H_2Dz$	2·31 ± 0·05	26·79[2]	29·1 (31·9)[5]
$Pb(HDz)_2 + 2HDDC = Pb(DDC)_2 + 2H_2Dz$	4·98 ± 0·05	0·76[2]	5·74 (7·77)[5]
$Pd(HDz)_2 + 2HDDC = Pd(DDC)_2 + 2H_2Dz$	1·6 ± 0·2	>27[2]	>29
$In(HDz)_3 + 3HDDC = In(DDC)_3 + 3H_2Dz$	4·75 ± 0·10	4·84[2]	9·59 (10·34)[5]
$As(DDC)_3 + H_2Dz = AsDzDDC + 2HDDC$	−7·93 ± 0·06		
$Sb(DDC)_3 + H_2Dz = Sb(HDz)(DDC) + HDDC$	−2·47 ± 0·07		
$Bi(DDC)_3 + 3H_2Dz = Bi(DDC)_3 + 3HDDC$	5·72 ± 0·08	10·76[2]	16·48 (16·79)[5]
$Se(HDz)_4 + 4HDDC = Se(DDC)_4 + 4H_2Dz$	~6·5		
$Te(HDz)_4 + 4HDDC = Te(DDC)_4 + 4H_2Dz$	~5·5		

* The errors quoted are the standard errors of the means.

constants, are in general in the agreement with the values determined by the solvent extraction method.

It was shown that by the change of the organic solvent the exchange constant changes, in dependence on the distribution coefficients of metal chelate and organic reagent used.

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Zusammenfassung—Dithizonate und Diäthyldithiocarbamate von Ag, Tl(I), Cu(II), Zn, Cd, Hg(II), Pb, Fe(II), Co(II), Ni, Pd(II), In(III), As(III), Sb(III), Bi, Se(IV) und Te(IV) wurden dargestellt und ihre Reaktionen in Tetrachlorkohlenstoff spektrophotometrisch untersucht. Aus den gemessenen Austauschkonstanten wurden die Extraktionskonstanten der Metall-Diäthyldithiocarbamate berechnet. Für die Fälle, in denen Bildung gemischter Chelate beobachtet wurde, wurden entsprechende Austauschkonstanten bestimmt. Endlich wurde der Einfluß organischer Lösungsmittel (CCl_4, $CHCl_3$, C_6H_6 und C_6H_5Cl) auf die Austauschreaktion zwischen Zinkdiäthyldithiocarbamat und Dithizon untersucht.

Résumé—On a préparé les dithizonates et les diéthyldithiocarbamates de Ag, Tl(I), Cu(II), Zn, Cd, Hg(II), Pb, Fe(II), Co(II), Ni, Pd(II), In(III), As(III), Sb(III), Bi, Se(IV) et Te(IV) et l'on a étudié spectrophotométriquement leurs réactions en tétrachlorure de carbone. Des constantes d'échange déterminées, on a calculé les constantes d'extraction des diéthyldithiocarbamates métalliques. Lorsqu'on a observé la formation de chélates mixtes, on a déterminé les constantes d'échange correspondantes. Finalement, on a étudié l'influence de solvants organiques (CCl_4, $CHCl_3$, C_6H_6 et C_6H_5Cl) sur la réaction d'échange du diéthyldithiocarbamate de zinc avec la dithizone.

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METAL ION SEPARATIONS USING CELLULOSE PHOSPHATE AS AN ION-EXCHANGER

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Summary—Cellulose phosphate is used as a chelating ion-exchanger to effect the separation of several metal ions. Its exchange rate is much more rapid than that of a chelating ion-exchanger containing phosphonic acid groups on a polystyrene matrix. Weight distribution coefficients as a function of hydrogen ion concentration on cellulose phosphate are given for several metal ions. Successful separations of rare earths and alkaline earths, alkaline earths and alkali metals and aluminium and alkaline earths have been achieved on cellulose phosphate columns.

THE success of bis(2-ethylhexyl)orthophosphoric acid and related compounds for analytical separations of metal ions suggests the possibility of using columns packed with resinous materials containing a chemically bonded phosphoric acid group for separations. Such a material should be more rugged and easier to work with than is the case when a complexing ligand is merely sorbed onto a solid support. Phenol–formaldehyde copolymers have been prepared in which arsenious acid, phosphonic acid or phosphoric acid groups have been incorporated.[1] Phosphate and phosphonate groups have also been placed on other organic matrices.[2–7] These resins tend to have a high selectivity for those metals which form phosphate complexes. Some column separations have been carried out with these resins.[8–10]

Cellulose phosphate is another polymeric material that contains an acidic phosphate group which might be expected to complex metal ions selectively. Although this material has been used rather extensively for biochemical separations, very little has been published regarding its possible use as a chelating ion-exchanger for separation of metal ions. Head *et al.* have published a paper on the general properties of this exchanger.[11] Cellulose phosphate has been used in paper chromatographic systems,[12–14] as well as in column separations of uranium from other metals,[15,16] iron(III) from copper(II) and nickel(II),[14] caesium(I) from strontium(II)[17] and the recovery of thorium from monazite ores.[18]

In the present research, cellulose phosphate is shown to have definite advantages over a synthetic polymeric phosphonic acid for the separation of metal ions. By use of eluents containing dilute hydrochloric acid, quantitative column separations of rare earths or aluminium from alkaline earths and of alkaline earths from alkali metal ions may be accomplished.

EXPERIMENTAL

Reagents

Chelating ion-exchangers. Whatman cellulose phosphate, P 11, purchased from H. Reeve Angel and Co. Inc., Clifton, N.J., was prepared according to the directions for precycling given in Whatman's

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† Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 2161.

technical bulletin C5.[19] Larger amounts of exchanger could be prepared in this way, and kept for several days without any appreciable hydrolysis by removing the supernatant 0·5*M* hydrochloric acid, washing the exchanger several times with demineralized water and then keeping it in the demineralized water until ready for use.

Bio-Rex 63, which has phosphonic acid groups on a polystyrene matrix, was obtained in 100–200 mesh size in the sodium form from the Bio-Rad Laboratories, Richmond, California. The resin was back-washed in a column to remove all fines, and then enough 1*M* hydrochloric acid was passed through it to convert it into the hydrogen form. The resin was then washed with demineralized water and allowed to dry in air. It was used in this form for all experiments.

Metal ion solutions. The metal ion solutions were prepared from reagent grade nitrate or chloride salts, except in the case of rare earth solutions which were prepared from the oxides. They were dissolved in water with sufficient acid present to insure complete dissolution and to prevent hydrolysis.

EDTA. The 0·05*M* and 0·01*M* EDTA solutions were prepared from reagent grade disodium salt and were standardized with standard zinc(II) solution, Naphthyl Azoxine S(NAS) being used as the indicator.[20]

Apparatus

Columns. Conventional 1 × 15 cm, coarse frit chromatographic columns with teflon stop-cocks were used for all separations. The tips of the columns were cut off just below the stop-cock in order to eliminate tip hold-up volume. The flow-rate of the eluents in all separations was regulated with compressed air. A one-hole rubber stopper with a short piece of glass tubing through it was inserted at the top of the column. This tubing was connected to a compressed-air line through a Johnson regulator.

Scintillation counter. A Nuclear-Chicago single channel analyser, model No. 27352, with a six decade electronic scaler and a 3 × 3 in. sodium iodide, thallium-activated, crystal was used to isolate and count the gamma emission of the radioactive ions.

Atomic absorption spectrophotometer. A Perkin–Elmer atomic absorption spectrophotometer, model No. 303, was used to analyse for lithium, potassium and rubidium.

Procedure

Methods of analysis. Calcium(II). Any hydrolysed phosphate from the cellulose phosphate was removed by passing the solution containing the calcium through a 1 × 5·7 cm column containing 100–200 mesh, cation-exchange resin (Dowex 50 × 8) at a flow-rate of 2–3 ml/min. The column was washed with 50 ml of water to ensure all the phosphate had been removed and then the calcium was stripped with 25 ml of 4*M* nitric acid. The calcium was determined by spectrophotometric titration at 572 mμ with 0·01*M* EDTA, with Metalphthalein as the indicator.[21]

Magnesium(II), strontium(II), aluminium(III), cobalt(II), nickel(II) and the rare earths. These ions were determined by standard EDTA titration methods.

Lithium(I), potassium(I) and rubidium(I). These three alkali metals were determined by atomic absorption spectrophotometry

Other elements. All other elements were determined by counting their gamma emissions with a scintillation counter.

Determination of weight distribution coefficients

Approximately equal amounts of the wet precycled cellulose phosphate (1 ± 0·3 g) were combined with 20 ml of a known concentration of hydrochloric acid solution and a known amount of metal ion. This mixture was shaken for at least 30 min and then filtered. The filtrate was analysed for metal ion content and acidity. The weight of the cellulose phosphate was determined by drying at 95–100° until constant weight was obtained. From these data, the weight distribution coefficients were determined. It was decided that it would be easier and safer in the case of the radioactive trace samples, to weigh a known amount of air-dried cellulose phosphate and to convert it to its dried weight by applying the moisture factor of 6·8%. It was assumed that since trace amounts of metal ion were being used (less than 0·1% of nominal capacity), the absence of precycling would have no effect on the weight distribution coefficients.

The weight distribution coefficients as a function of hydrochloric acid concentration for lanthanum(III) on Bio-Rex 63 were determined according to standard ion-exchange procedures.

Column packing

Enough precycled cellulose phosphate for four columns was slurried in the eluant to be used in the separation. The slurry was added to the columns and packed under 5 psi air-pressure. A glass-wool plug was placed on top of the exchanger to prevent it from floating during the elution.

Separation procedure

The samples were placed on the column by means of a pipette or were quantitatively transferred from a 10-ml beaker. The sample volumes varied between 1 and 8 ml. After the samples were placed on the column, elution was carried out under an air-pressure of 2 or 3 psi in order to obtain flow-rates of 0·8–1·5 ml/min. After the first metal ion was completely off the column, the eluent was changed and the next metal ion was eluted from the column. If after the last element was eluted, the column was immediately washed with the less acidic eluent, it could be used again without any noticeable deterioration of the column.

RESULTS AND DISCUSSION

Selection of the exchanger

The two ion-exchangers investigated were the commercially available Bio-Rex 63, containing phosphonate groups on a polystyrene matrix, and Whatman P11 cellulose phosphate. These exchangers were compared first by weight distribution coefficients (D_W) as a function of hydrogen ion concentration for lanthanum(III), and second, by the rate at which they attained equilibrium with lanthanum(III) in a 0·5*M* hydrochloric acid solution. In the kinetics experiment, weight distribution coefficients $(D_W)_t$ were determined at timed intervals and compared with the weight distribution coefficient at equilibrium $(D_W)_{eq}$. The results are shown in Fig. 1. The results for the weight distribution coefficients (D_W) as a function of hydrogen ion concentration are shown in Fig. 2. These results show that the kinetics of the cellulose phosphate exchange are much faster and that lanthanum has higher weight distribution coefficients on it. It was also found that Bio-Rex 63 undergoes large volume changes with small changes in acidity, which was not found with the cellulose phosphate. For these reasons, cellulose phosphate was chosen for all subsequent experiments.

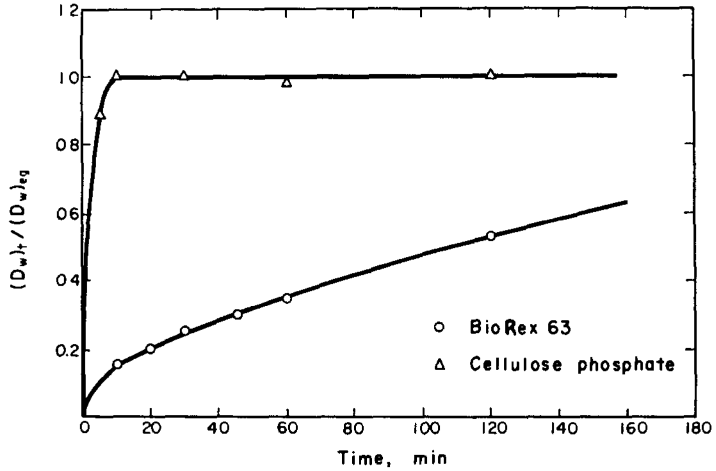

FIG. 1.—Comparison of the rate at which Bio-Rex 63 and cellulose phosphate attain equilibrium for lanthanum(III) from hydrochloric acid solution.

Effect of loading

Loading is an important factor in all ion-exchange separations because the weight distribution coefficient depends directly on the extent of loading. The nominal capacity of cellulose phosphate, including the weakly and strongly acidic hydrogen atoms, is 7·4 meq/g. In order to find the range of loading that could be tolerated, the weight distribution coefficients in 0·5M hydrochloric acid were determined at various degrees of loading. The results are shown in Fig. 3. The weight distribution coefficient at trace loading is shown as $(D_w)_t$. From the results, it can be seen that the maximum weight distribution coefficient occurs at a loading capacity of less than 2·0% of nominal capacity. In all subsequent investigations, the loading was kept below this value when at all possible.

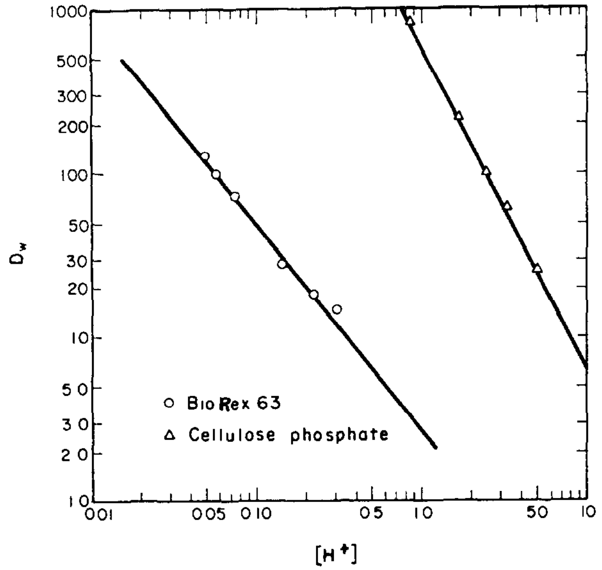

FIG. 2.—Comparison of weight distribution coefficients as a function of hydrochloric acid concentration for lanthanum(III) on Bio-Rex 63 and cellulose phosphate.

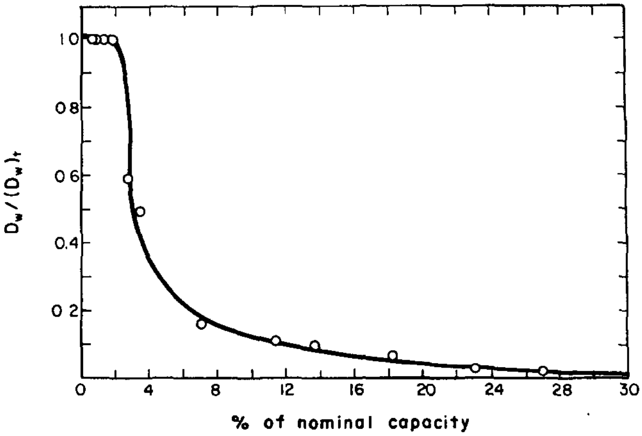

FIG. 3.—Effect of loading on the weight distribution coefficient on cellulose phosphate of lanthanum(III) from hydrochloric acid solution.

Weight distribution coefficients

The weight distribution coefficients as a function of hydrogen ion concentration for several metal ions on cellulose phosphate are shown in Figs. 4 and 5. In addition

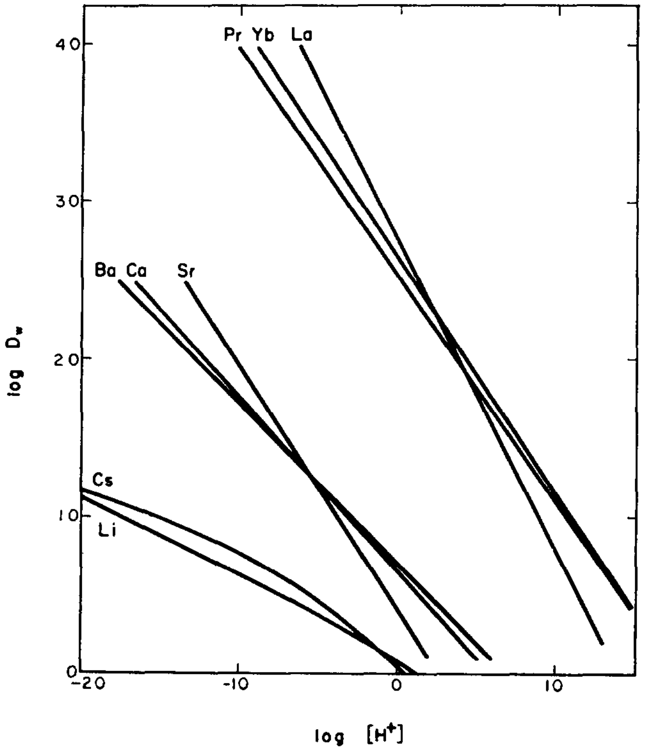

FIG. 4.—Weight distribution coefficients as a function of hydrochloric acid concentration on cellulose phosphate.

to the elements shown, it was found that erbium has almost the same weight distribution coefficients as ytterbium, magnesium has approximately the same as strontium, and the curves for potassium and rubidium lie between those shown for a caesium and lithium. From these results, it can be seen that the behaviour of the four representative rare earths, the alkaline earths, and the alkali metals is nearly identical in each respective group, but there are great differences among the groups as a whole. The variation in slopes within each group is probably due to failure to maintain constant ionic strength.

The weight distribution coefficients for the rare earths and aluminium are extraordinarily high for an intermediate acidic ion-exchanger, even in quite high acidity. This phenomenon may very well be explained by the fact that they form strong phosphate complexes. Head *et al.* also found this to be true for other ions, such as uranium(VI), iron(III), and thorium(IV), which also form strong phosphate complexes.[11] The alkaline earths, alkali metals, nickel, cobalt and chromium, however, seem to possess weight distribution coefficients of the magnitude that would be expected for ordinary ion-exchangers of intermediate acidic strength.

A plot of the logarithm of the weight distribution coefficient (D_w) against the logarithm of the hydrogen ion activity should give a negative slope (n) equal to the number of hydrogen ions replaced from the ion-exchanger. Constant ionic strength was maintained by addition of lithium chloride to the hydrochloric acid solutions. The

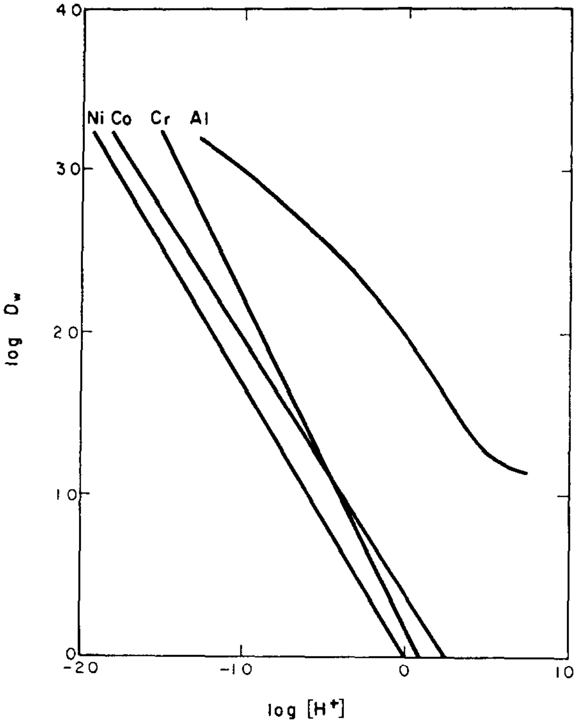

FIG. 5.—Weight distribution coefficients as a function of hydrochloric acid concentration on cellulose phosphate for nickel(II), cobalt(II), chromium(III), and aluminium(III).

solutions were kept at 1·5*M* total chloride for barium-133 and strontium-85 and 2·0*M* for europium-152-154. The metals were in trace amounts and the cellulose phosphate was in large excess in order to keep the activity constant. The results are straight-line plots and show that the number of hydrogen ions replaced in the case of barium and strontium is 1·03 ± 0·01, and for europium is 1·34. Head *et al.* found also that for thorium(IV) less than the equivalent number of hydrogen ions was displaced.[11] In an analogous system of Kel-F impregnated with bis(2-ethylhexyl)orthophosphoric acid, Lieser and Berhard obtained an *n* of 1·0 ± 0·1 for calcium(II) and strontium(II).[22] Cerrai and Ghersini also found that the number of hydrogen ions replaced in a paper chromatographic system employing bis(2-ethylhexyl)orthophosphoric acid was less than the charge on the ion for many elements.[23] Although these results indicate the possibility of mixed complexes on cellulose phosphate, the exact nature of these complexes cannot be determined without more experimental evidence.

Separations

The actual behaviour of the cellulose phosphate column was compared with that which would be predicted from plate theory for the elution of trace amounts of barium-133 with 0·5*M* hydrochloric acid. The effective HETP was calculated from the column length and the relationship $N = 8(V_R/\beta)^2$, where N is the number of theoretical plates, V_R is the retention volume, and β is the width of the elution curve (in ml) at the concentration $c = c_{max}/e = 0{\cdot}368c_{max}$. In this case, the effective HETP was found to be 3·6 mm. The volume distribution coefficient (D_V) was calculated from the relationship $V_R/X' = D_V + \varepsilon$, where X' is the column volume corrected for sample volume and ε is the void fraction. D_V was found to be 2·66. The D_V was then calculated from the relationship $D_V = D_W Q_R$, where Q_R is the column density, and the value found was 2·61. Since the column was packed the same for all separations, the column density was assumed to remain relatively constant. Therefore, approximate volume distribution coefficients could be determined from weight distribution coefficients using the relationship described above. Using these values and the values for the separation factors, appropriate conditions for metal ion separations were chosen.

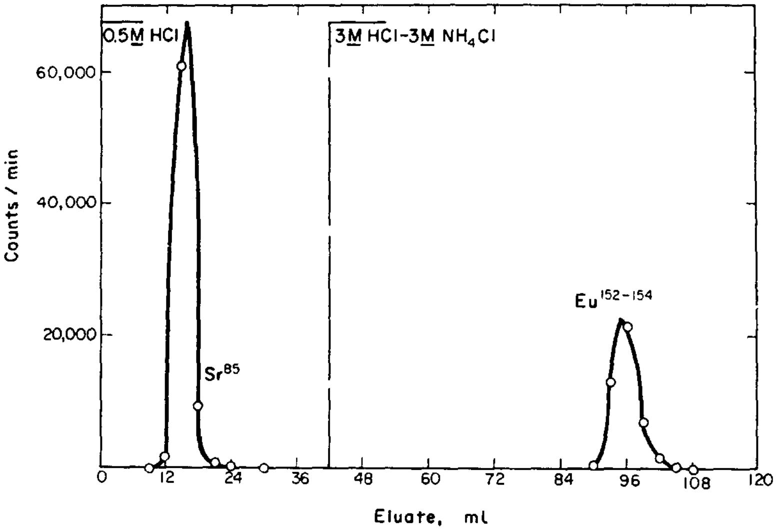

Fig. 6.—Elution curve for strontium(II) and europium(III) from a cellulose phosphate column. Column: 1 × 7·0 cm; flow-rate: 1·2 ± 0·2 ml/min; sample volume: 2·0 ml; strontium(II): $1\cdot7 \times 10^{-4}$ μmole; europium(III): $6\cdot3 \times 10^{-6}$ μmole.

Successful separations of rare earths from alkaline earths were carried out. The alkaline earth was eluted with 0·5*M* hydrochloric acid and the rare earth was stripped with either 3*M* hydrochloric acid–3*M* ammonium chloride solution or 7*M* hydrochloric acid. It was decided that the 3*M* hydrochloric acid–3*M* ammonium chloride solution was the best eluent because it removes the metal as efficiently as 7*M* hydrochloric acid but without causing as much hydrolysis. A typical elution curve is shown in Fig. 6.

Separations of caesium(I) and strontium(II) with 0·1*M* hydrochloric acid as the eluent were also carried out. An elution curve for one of the separations is shown in Fig. 7. A quantitative separation of europium(III), strontium(II) and caesium(I) was performed using 0·1*M* hydrochloric acid to elute the caesium(I) and strontium(II) followed by 3*M* hydrochloric acid–3*M* ammonium chloride solution to elute the europium(III). A separation of aluminium(III) from strontium(II) was achieved by using 0·05*M* hydrochloric acid to elute the strontium(II), followed by 4*M* hydrochloric acid to elute the aluminium(III).

Because aluminium and magnesium commonly occur in several alloys, a synthetic mixture of the two was prepared by dissolving the pure metals in hydrochloric acid.

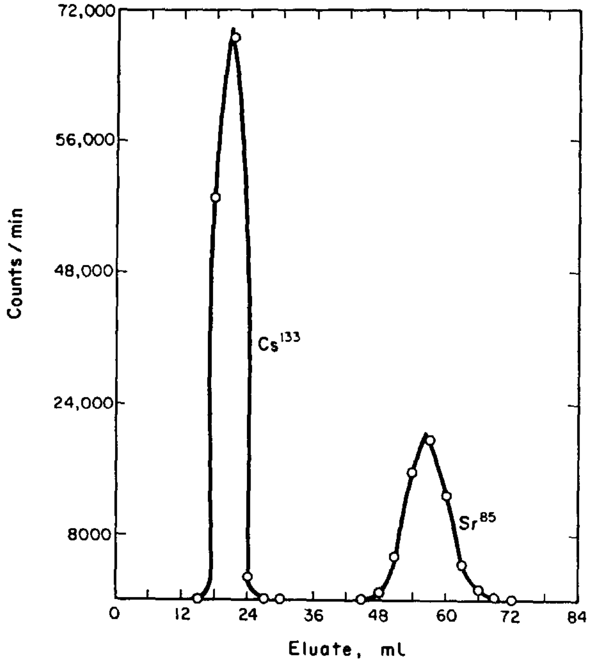

Fig. 7.—Elution curve for caesium(I) and strontium(II) from a cellulose phosphate column with 0·1*M* hydrochloric acid as the eluent. Column: 1 × 7·6 cm.; flow-rate: 1·2 ± 0·2 ml/min; sample volume: 2·0 ml; caesium(I): 2·7 μmole; strontium(II): 1·7 × 10^{-4} μmole.

Table I.—Results of the separations of rare earths, aluminium, alkaline earths, and alkali metals on 1-cm i.d. cellulose phosphate columns

Sample	Metal-ion	Taken, *μmole*	Recovery, %	Column length, *cm*	Eluate, *ml*
La–Ca	La(III)	214·8	100·0	14·6	65
	Ca(II)	105·8	100·0		55
La–^{133}Ba	La(III)	100·9	99·7	11·2	65
	^{133}Ba(II)	1·9 × 10^{-4}	98·8		50
$^{152-154}$Eu–^{85}Sr	$^{152-154}$Eu(III)	6·3 × 10^{-6}	96·2	7·0	66
	^{85}Sr(II)	1·7 × 10^{-4}	99·8		42
$^{152-154}$Eu–^{85}Sr	$^{152-154}$Eu(III)	91·4	99·3	7·0	33
	^{85}Sr(II)	1·7 × 10^{-4}	99·5		36
$^{152-154}$Eu–^{85}Sr	$^{152-154}$Eu(III)	6·3 × 10^{-6}	98·4	7·2	63
	^{85}Sr(II)	1239	100·7		36
^{134}Cs–^{85}Sr	^{134}Cs(I)	2·7	100·8	7·6	30
	^{85}Sr(II)	1·7 × 10^{-4}	100·6		75
^{134}Cs–^{85}Sr	^{134}Cs(I)	2·7	100·5	10·2	27
	^{85}Sr	1017	100·8		78
$^{152-154}$Eu–^{85}Sr–^{134}Cs	$^{152-154}$Eu(III)	2·7	100·3		72
	^{85}Sr(II)	1·7 × 10^{-4}	100·8	13·6	99
	^{134}Cs(I)	100·9	100·3		45
Al–^{85}Sr	Al(III)	99·3	99·9	13	75
	^{85}Sr(II)	129·3	100·6		45
Al–Mg	Al(III)	111·8	100·1	14	150
	Mg(II)	98·6	100·0		45

Then aliquots of this sample were separated by using 0·5*M* hydrochloric acid to elute the magnesium(II), followed by 4*M* hydrochloric acid to elute the aluminium(III). The results for this separation and those previously discussed are shown in Table I.

It was felt that the cellulose phosphate system could be combined with other separation systems. In order to demonstrate this point, two synthetic samples, one containing uranium, erbium and magnesium, and the other containing uranium, aluminium and nickel, were prepared from the pure metals. In both samples, the uranium was separated from the other elements on a 1 × 15 cm, 80–100 mesh silica gel column in a 6*M* acid–isobutylmethyl ketone system and the other elements were stripped from the column with demineralized water.[24] In the first sample, the eluate contained the magnesium and erbium. It was diluted with water until its acidity was 1*M* (approximately 40 ml). This solution was then passed through a 1 × 14 cm cellulose phosphate column, and to ensure complete removal of the magnesium(II) the column was subsequently washed with 25 ml of 1*M* hydrochloric acid. The erbium(III) was stripped with 100 ml of 3*M* hydrochloric acid–3*M* ammonium chloride solution. In the second sample, the eluate containing the aluminium and nickel was adjusted to 0·5*M* in acidity by adding a few drops of ammonium hydroxide and diluting the sample to about 40 ml. This solution was passed through a 1 × 14·2 cm cellulose phosphate column and subsequently washed with 35 ml of 0·5*M* hydrochloric acid to ensure complete removal of all the nickel(II). The aluminium(III) was removed with 100 ml of 4*M* hydrochloric acid. The average results of four separations for each sample are given in Table II.

TABLE II.—RESULTS OF SEPARATIONS OF SAMPLES, BOTH SILICA GEL AND CELLULOSE PHOSPHATE COLUMNS BEING USED

Sample	Metal ion	Taken, *μmole*	Found, *μmole*	Difference, *μmole*
U–Er–Mg	U(VI)	305·2	306·1	+0·5
	Er(III)	99·6	99·4	−0·2
	Mg(II)	102·7	103·2	+0·5
U–Al–Ni	U(VI)	406·8	407·3	+0·5
	Al(III)	212·8	212·2	−0·6
	Ni(II)	86·8	86·8	0·0

Zusammenfassung—Cellulose phosphat wird als chelatbildender Ionenaustauscher zur Trennung mehrerer Metallionen verwendet. Sein-Austauschgeschwindigkeit ist viel gröser als die eines chelatbildenend Ionenaustauschers mit Phosphonsäuregruppen an einem Polystyrolgerüst. Für mehrere Metallionen werden Gewichtsverteilungskoeffizienten an Cellulosephosphat in Abhängigkeit von der Wasserstoffizienkonzentration angegeben. Auf Cellulosephosphatsäulen gelangen Trennungen von seltenen Erden und Erdalkalien, Erdalkalien und Alkalimetallen sowie von Aluminium und Erdalkalien.

Résumé—On utilise le phosphate de cellulose comme échangeur d'ions chélatant pour effectuer la séparation de différents ions métalliques. Sa vitesse d'échange est beaucoup plus rapide que celle d'un échangeur d'ions chélatant contenant des groupements acide phosphonique sur un squelette polystyrène. On donne les coefficients de distribution en pods en fonction de la concentration en ion hydrogène pour différents ions métalliques sur phosphate de cellulose. On a réalisé avec succès, sur des colonnes de phosphate de cellulose, des séparations de terres rares et d'alcalino-terreux, d'alcalino-terreux et de métaux alcalins et d'aluminium et d'alcalino-terreux.

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SPECTROPHOTOMETRIC STUDY OF THE REACTION OF IRON(III) WITH METHYLTHYMOL BLUE

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Summary—The reaction between iron(III) and Methylthymol Blue (MTB or H_6A) has been investigated by spectrophotometry. It has been established that iron(III) and MTB form two complexes with compositions iron(III): MTB = 1:1 and 1:2. The 1:1 complex is stable in acidic medium containing excess of iron, and the 1:2 complex is stable in slightly acidic or alkaline media containing excess of MTB. The absorption maxima are at 610 mμ (1:1) and 515 mμ (1:2), the molar absorptivities being $1{\cdot}73 \pm 0{\cdot}01 \times 10^4$ and $3{\cdot}21 \pm 0{\cdot}05 \times 10^3$ respectively. The nature of the two complexes at pH 6 and the stability constants have been determined: $\log \beta_{11} = 20{\cdot}56 \pm 0{\cdot}07$, $\log \beta_{112} = 43{\cdot}29 \pm 0{\cdot}09$, $\log \beta_{12} = 6{\cdot}66 \pm 0{\cdot}05$.

METHYLTHYMOL BLUE, 3,3′-bis[N,N-bi(carboxymethyl)aminomethyl]thymosulphophthalein, (MTB or H_6A), was synthesized by Körbl[1] and has been applied as a complexometric indicator for the determination of a number of metal ions.[2] MTB is also used as a reagent for the photometric determination of zirconium,[3,4] thorium,[5,6] iridium,[7] lanthanum,[7–9] yttrium,[8,10] cerium,[8] indium,[11] mercury,[12] gallium,[13] magnesium,[14] aluminium[15] and hafnium.[16]

Iron(III) also forms coloured complexes with MTB. This reaction and its analytical application have been briefly discussed by Tihonov[17] and at greater length by Tonosaki,[18] but this work, in our opinion, contains several errors, probably because the investigations were made in the presence of an excess of MTB and over a limited range of pH.

We have studied this reaction in greater detail and can define more accurately the conditions for its spectrophotometric application.

EXPERIMENTAL

Reagents

Methylthymol Blue. The Chemapol product was used; it contained 7·9% water and 8·2% sodium; *i.e.*, it was the trisodium salt. Aqueous solutions of MTB last only for 2–3 days[14] which makes it imperative to work with a freshly prepared solution. The water content was allowed for in preparing the solutions, which were standardized by spectrophotometric titration with iron(III) at pH 4–5 and 610 mμ.

Iron(III) nitrate solution. Prepared by dissolving the solid salt in water and standardized gravimetrically. The $1{\cdot}042 \times 10^{-3}M$ working solution was obtained by precise dilution. To avoid hydrolysis, the solution was acidified to pH 2·5 with nitric acid.

Ionic strength. All investigations were carried out at a constant ionic strength of 0·1, maintained by addition of the required amount of 1*M* sodium perchlorate solution.

Buffers. The pH was controlled with 0·1 and 1*M* perchloric acid, acetate buffer solutions of pH 3·6–5·8, 20% hexamine solution and 0·01, 0·1 and 1*M* sodium hydroxide.

The reagents used were *pro analysi* grade.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of iron(III) nitrate solutions of constant concentration, containing various quantities of MTB at pH 5·1 and 12·0 are shown in Figs. 1 and 2. As can be seen from Fig. 1, curve 6, MTB in acidic medium has an absorption maximum at 440 mμ, and at pH 6·4 another maximum appears at 600 mμ (Fig. 2, curve 1). Addition of MTB to acidic solutions containing iron(III) gives rise to an absorption maximum at 610 mμ, which decreases when MTB is in excess, a new maximum then appearing at a shorter wavelength. The colour of the solution changes

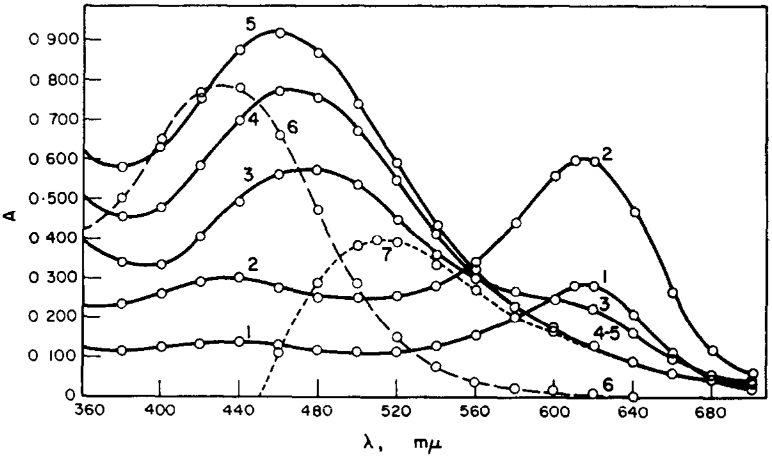

FIG. 1.—Absorption spectra at pH 5·0.
1-5 and 7—C_{Fe} = 4·17 × $10^{-5}M$. C_{H_6A}: 1—1·88 × $10^{-5}M$, 2—4·17 × $10^{-5}M$, 3—6.25 × $10^{-5}M$, 4, 6 and 7—8.34 $10^{-5}M$, 5—1.04 $10^{-4}M$.
From 1 to 6—water blank, 7—MTB blank.

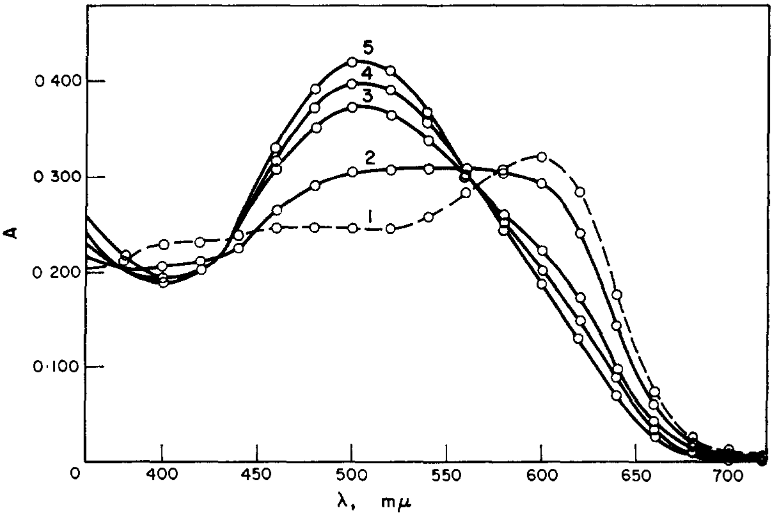

FIG. 2.—Absorption spectra at pH 12·0.
1-5—C_{H_6A} = 4·17 × $10^{-5}M$, C_{Fe}: 1—0, 2—8·34 × $10^{-6}M$, 3—1·67 × $10^{-5}M$, 4—2·08 × $10^{-5}M$, 5—2·51 × $10^{-5}M$.

from blue when iron is in excess to brown-red when MTB is in excess. The absorption maximum of the brown-red compound is at 515 $m\mu$ (Fig. 1, curve 7).

Only one maximum, at 515 $m\mu$, is observed in alkaline medium (Fig. 2) when the concentration of the iron is changed. The corresponding complex is red.

Composition of the complexes

The composition of the complexes formed between iron(III) and MTB was established by the methods of continuous variations and of mole-ratios.[19,20] The experiments were performed at various pH values and at two wavelengths.

Two complexes are formed, as can be seen from Figs. 3 and 4. The compound with an absorption maximum at 610 $m\mu$ is blue and has a composition Fe(III) : MTB = 1 : 1 while the compound which absorbs at 515 $m\mu$ is brown-red in acidic medium and red in alkaline medium, and has composition Fe : MTB = 1 : 2. We conclude from these results that the blue 1 : 1 compound is stable in acidic medium with excess of iron(III) present, and the less stable red-brown 1 : 2 compound is obtained in slightly acidic medium with an excess of MTB, and in alkaline medium no matter what the ratio of the reacting components.

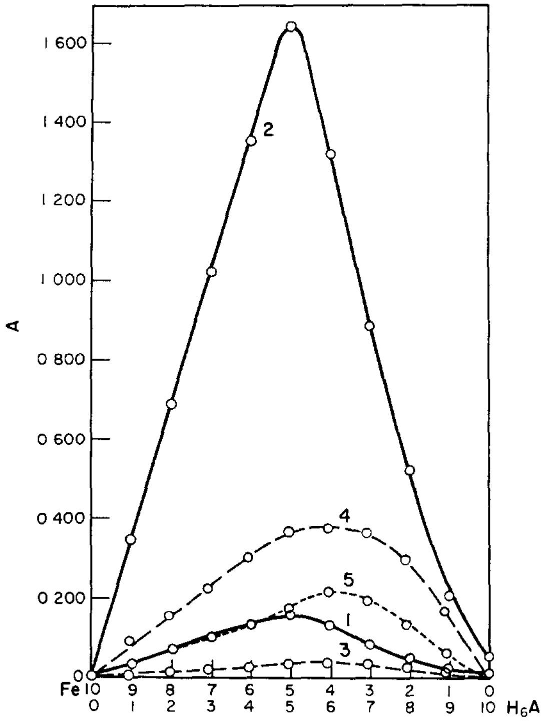

FIG. 3.—Method of continuous variation.
1, 2, 3 and 4 at pH 1·7; 5 at pH = 12. 1 and 2 at 610 $m\mu$; 3, 4 and 5 at 515 $m\mu$.
1 and 3 : $C_{Fe} + C_{H_6A} = 2{\cdot}08 \times 10^{-5}M$; 2 and 4 : $C_{Fe} + C_{H_6A} = 2{\cdot}08 \times 10^{-4}M$;
5 : $C_{Fe} + C_{H_6A} = 4{\cdot}17 \times 10^{-5}M$. 1 and 2—water blank, 3, 4 and 5—MTB blank.

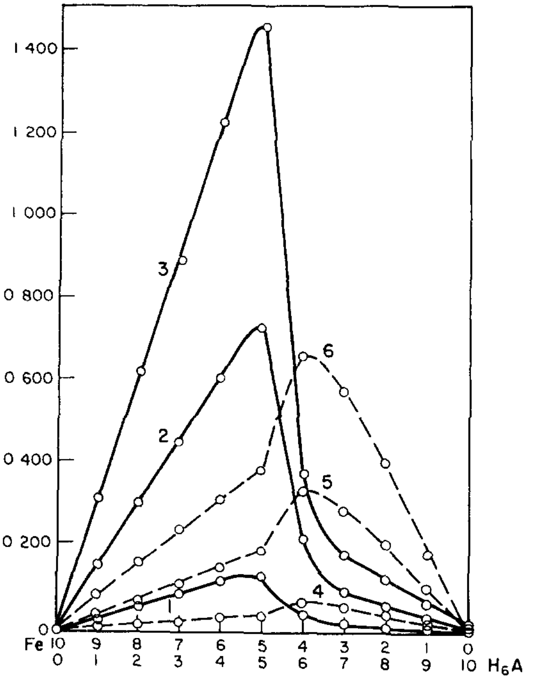

FIG. 4.—Method of continuous variations at pH 5·0.
1, 2 and 3 at 610 mμ; 4, 5 and 6 at 515 mμ. 1 and 4: $C_{Fe} + C_{H_6A} = 2{\cdot}08 \times 10^{-5}M$; 2 and 5: $C_{Fe} + C_{H_6A} = 1{\cdot}04 \times 10^{-4}M$; 3 and 6: $C_{Fe} + C_{H_6A} = 2{\cdot}08 \times 10^{-4}M$.
1, 2 and 3—water blank, 4, 5 and 6—MTB blank.

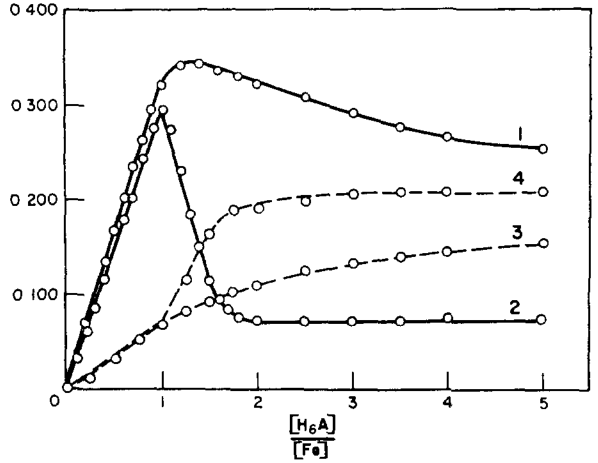

FIG. 5.—Mole-ratio method.
$C_{Fe} = 2{\cdot}08 \times 10^{-5}M$; 1 and 2 at 610 mμ; 3 and 4 at 515 mμ. 1 and 3 at pH 1·7; 2 and 4 at pH 5·0. 1 and 2—water blank, 3 and 4—MTB blank.

These conclusions are supported by the mole-ratio method results (Figs. 5 and 6). Curves 4 and 5 in Fig. 6 show that at pH 11 only the 1:2 complex is formed. In alkaline medium, any excess of iron(III) is precipitated as the hydrous oxide.

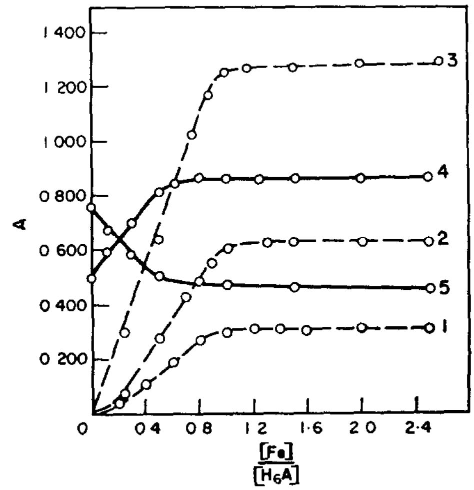

FIG. 6.—Mole-ratio method.
1, 2, 3 and 5 at 610 mμ; 4 at 515 mμ. 1, 2 and 3 at pH 1·7; 4 and 5 at pH 11·0. C_{H_6A}: 1—1·04 × $10^{-5}M$, 2—2·08 × $10^{-5}M$, 3—3·13 × $10^{-5}M$, 4 and 5—4·17 × $10^{-5}M$.

Degree of protonation of the complexes

The formation of the 1:1 complex can be expressed by the equation:

$$Fe^{3+} + H_{6-n}A^{n-} \rightleftharpoons [Fe(H_{6-n-m}A)]^{n+m-3} + mH^{+}. \qquad (1)$$

The number of hydrogen ions released during reaction was established by following the effect of pH change on the absorbance of solutions containing a tenfold excess of MTB (Fig. 7, curve 4) or iron(III) (Fig. 7, curve 3). The formation of the complex begins at about pH 0·4 and is complete by pH 1–1·2. The successive p*K* values of MTB are[1,10] 3·0, 3·3, 3·8, 7·4, 11·15 and 13·4, so about 99% of the MTB is present as H_6A at pH = 1·0, and *n* in equation (1) is zero.

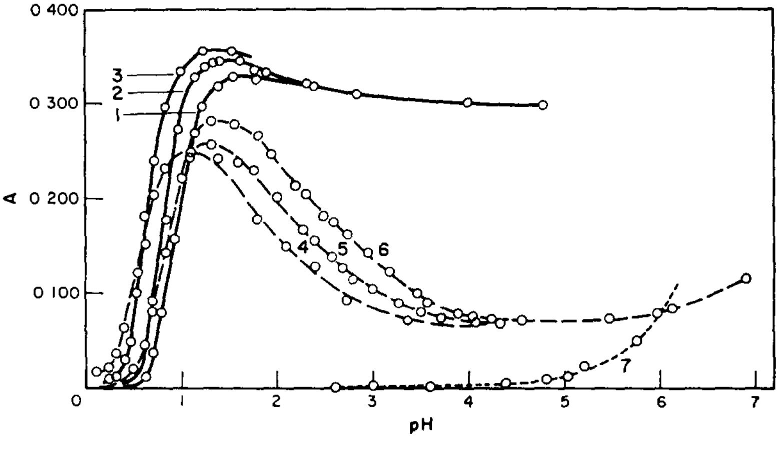

FIG. 7.—Absorbance as function of pH, at 610 mμ
C_{Fe}: 1—2·08 × $10^{-5}M$, 2—4·17 × $10^{-5}M$, 3—2·08 × $10^{-4}M$, 4, 5 and 6—2·08 × $10^{-5}M$. C_{H_6A}: 1, 2 and 3—2·08 × $10^{-5}M$, 4—2·08 × $10^{-4}M$, 5—8·33 × $10^{-5}M$, 6—4·17 × $10^{-5}M$, 7—1·04 × $10^{-4}M$.

If it is assumed that with a tenfold excess of MTB present the free MTB concentration is constant and can be set equal to the total analytical concentration of MTB, C_{H_6A}, then

$$\log \frac{[Fe(H_{6-m}A)]}{[Fe]} = m\text{pH} + \log K.C_{H_6A} \tag{2}$$

when K is the equilibrium constant for reaction (1). Log $K.C_{H_6A}$ is a constant, and a plot of log $\{A_{FeH_6A}/[Fe]\}$ against pH gives a straight line with slope m. A similar argument applies when iron(III) is in tenfold excess. The experimental slopes (Fig. 8, *a* and *b*) were 4·0 and 4·15 respectively, so it can be assumed that $m = 4$.

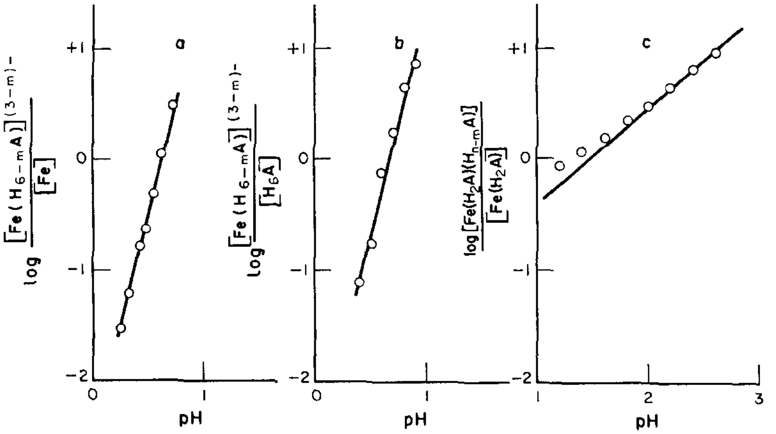

FIG. 8.—Dependence of the logarithm of the degree of complex formation (*a* and *b*) and the degree of transformation of the complex (*c*) on pH.
C_{Fe}: *a* and *c*—2·08 × $10^{-5}M$, *b*—2·08 × $10^{-4}M$. C_{H_6A}: *a* and *c*—2·08 × $10^{-4}M$, *b*—2·08 × $10^{-5}M$.

The degree of protonation of the MTB in the 1:1 complex can also be determined by finding the value of $(6 - m)$. If we write the dissociation of the complex as

$$[Fe(H_{6-m}A)] \rightleftharpoons Fe + H_{6-m}A, \tag{3}$$

omitting charges for simplicity, then the stability constant β_{11} is given by

$$\beta_{11} = \frac{[Fe(H_{6-m}A)]}{[Fe][H_{6-m}A]} = \frac{[Fe(H_{6-m}A)]}{[Fe][A][H]^{6-m}\beta_{H_{6-m}A}} \tag{4}$$

where $\beta_{H_{6-m}A}$ is the overall stability constant for $H_{6-m}A$. If $C_{Fe} > C_{H_6A}$, the degree of formation of the complex, α, can be expressed by

$$\alpha = \frac{A}{A_{\max}} = \frac{[Fe(H_{6-m}A)]}{C_{H_6A}} \tag{5}$$

where A is the absorbance at a given pH, and $A_{\max}$ is the maximum absorbance, corresponding to the completely associated complex.

The equilibrium concentrations of iron(III), MTB and the complex can be expressed by means of the total concentrations and the degree of formation of the complex under the conditions that there is an excess of iron(III) and that $[H_6A] \gg [H_5A]$. Then if $a = C_{Fe}/C_{H_6A}$; $[Fe(H_{6-m}A)] = \alpha C_{H_6A}$; $[Fe] = C_{H_6A}$; $[H_6A] = C_{H_6A}(1 - \alpha)$, then substitution in equation (4) gives

$$\frac{\alpha f_A}{(a - \alpha)(1 - \alpha)C_{H_6A}[H]^{6-m}\beta_{H_{6-m}A}} = \frac{Zf_A}{C_{H_6A}[H]^{6-m}\beta_{H_{6-m}A}} \tag{6}$$

where $Z = \alpha/(a - \alpha)(1 - \alpha)$, and $1/f_A$ is the fraction of uncomplexed MTB in the form A^{6-}.

From equation (6),

$$\log Zf_A = (m - 6)\,\text{pH} + B \tag{7}$$

where $B = \log \beta_{11}\beta_{H_{6-m}A}C_{H_6A}$ = a constant.

It is seen from equation (7) that a graph of log Zf_A *vs.* pH is a straight line, with slope $(6 - m)$, that is, the number of hydrogen ions associated with A in the complex. Figure 7 (curve 2) shows the dependence of the absorbance at 610 mμ on the pH at a ratio $C_{Fe}:C_{H_6A} = 2:1$, and Fig. 9 shows the dependence of log Zf_A on pH. The slope of Fig. 9 is -2, corresponding to $m = 4$. The absorbance of the free ligand is negligible under these conditions.

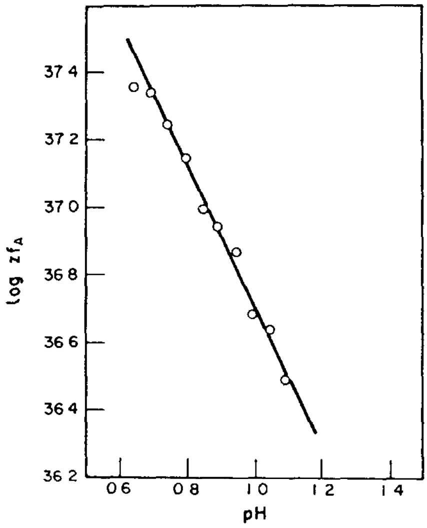

FIG. 9.—Dependence of log Zf_A on pH.

The formation of the 1:2 complex can be expressed by means of the equation

$$Fe(H_2A)^- + H_nA^{n-6} \rightleftharpoons Fe(H_2A)(H_{n-m}A)^{(n-m-7)} + mH^+. \tag{8}$$

The formation of this complex begins at pH 1·1–1·3 and is complete at pH 3·5–4 (curves 4, 5 and 6, Fig. 7). The number of protons released, m, in the reaction can be determined by plotting the absorbance at 610 mμ against pH, when MTB is in a great excess so that C_{H_6A} can be accepted as constant. Equation (8) gives

$$\log\,[Fe(H_2A)(H_{n-m}A)]/[Fe(H_2A)] = m\text{pH} + \log K.C_{H_6A} \tag{9}$$

where $\log K.C_{H_6A}$ is a constant.

This is an equation of a straight line with slope m, which is found (Fig. 8) to be $\sim$0·9. Taking into account that H_5A begins to dominate at pH $\sim$ 3, formation of the 1:2 complex can be expressed by

$$Fe(H_2A)^- + H_5A^- \rightleftharpoons Fe(H_2A)(H_4A)^{3-} + H^+ \rightleftharpoons Fe(H_3A)_2{}^{3-} + H^+. \tag{10}$$

In a strongly alkaline medium (at pH 13–14) the 1:2 complex undergoes destruction. This is shown by the decrease in the maximum at 515 mμ characteristic of the 1:2 complex and the appearance of a maximum at 600 mμ characteristic of the anion A^{6-}.

CALCULATION OF THE STABILITY CONSTANTS

If it is assumed that the 1:1 complex dissociates in the following way:

$$Fe(H_2A)^- \rightleftharpoons Fe^{3+} + H_2A^{4-}, \tag{11}$$

its stability constant can be calculated by the equation:

$$\beta_{11} = \frac{[Fe(H_2A)]}{[Fe][H_2A]} = \frac{[Fe(H_2A)].f_{H_2A}}{[Fe]\sum[H_nA]} \tag{12}$$

where $\sum[H_nA]$ is the total concentration of uncomplexed MTB species.

The value of this constant was calculated from the curves in Fig. 7 which express the change of absorbance with pH at differing ratios of iron(III) and MTB concentration.

A statistical treatment of 24 results gives at the 95% confidence limits the value of 20·56 ± 0·07 for log β_{11}.

The stability constant β_{112} based on the equation

$$Fe(H_2A^-) \rightleftharpoons Fe^{3+} + A^{6-} + 2H^+ \tag{13}$$

can be calculated from

$$\beta_{112} = \frac{[Fe(H_2A)]}{[Fe][H]^2[A]} = \frac{[Fe(H_2A)].f_A}{[Fe][H]^2\sum[H_nA]} \tag{14}$$

and has the value log $\beta_{112} = 43{\cdot}29 \pm 0{\cdot}09$ (95% confidence limits).

The stability constant of the 1:2 complex was calculated on the basis of the equation

$$Fe(H_3A)_2{}^{3-} \rightleftharpoons Fe(H_2A)^- + H_4A^{2-} \tag{15}$$

$$\beta_{12} = \frac{[Fe(H_3A)_2]}{[Fe(H_2A)][H_4A]} = \frac{[Fe(H_3A)_2].f_{H_4A}}{[Fe(H_2A)].\sum[H_nA]} \tag{16}$$

The equilibrium concentrations of $[Fe(H_3A)_2]$, $[Fe(H_2A)]$ and $\sum[H_nA]$ are calculated from curves 4, 5 and 6 of Fig. 7. As can be seen from these curves, there is a high absorbance at low pH, due to the 1:1 complex, but with increasing pH the curve passes through a maximum which corresponds to the 1:2 complex being formed. The part of the curve which shows a decrease in absorbance with increase in pH is used to calculate the equilibrium concentrations of the two complexes and the free MTB. The part of the curve showing constant absorbance with increasing pH corresponds to complete formation of the 1:2 complex.

The equilibrium concentrations of the two complexes are found by solving the set of equations

$$A = \varepsilon_1[\mathrm{Fe(H_2A)}] + \varepsilon_2[\mathrm{Fe(H_3A)_2}] \qquad (17)$$

$$C_{\mathrm{Fe}} = [\mathrm{Fe(H_2A)}] + [\mathrm{Fe(H_3A)_2}] \qquad (18)$$

where ε_1 and ε_2 are the molar absorptivities of the 1:1 and 1:2 complexes at 610 mμ. In equation (17) the absorbance of the free MTB is neglected since it is almost equal to zero (curve 6, Fig. 1), and in equation (18) the concentration of the free iron(III), which is very small in comparison with that of the complexed iron(III), is also ignored. The value of ε_1 at 610 mμ is determined from the absorbance of a solution containing a tenfold excess of iron(III) at pH 1·2. Its value is $1\cdot73 \pm 0\cdot01 \times 10^4$. That of ε_2 was determined by the same method but with MTB in excess at pH 4–5; it is $3\cdot21 \pm 0\cdot05 \times 10^3$.

The stability constant of the second complex had the value $\beta_{12} = 6\cdot66 \pm 0\cdot05$ (95% confidence limits, 36 results).

ANALYTICAL APPLICATION

The reaction of MTB with iron(III) can be used for the spectrophotometric determination of MTB or iron(III), as shown by Tonasaki;[18] the conditions he laid down are supported by the present work. The influence of some masking substances on the spectrophotometric determination of iron has been examined in the work of Tihonov.[17] The best conditions for spectrophotometric titration are pH 3–5·5 and wavelength 610 mμ.

Zusammenfassung—Die Reaktion zwischen Eisen(III) und Methylthymolblau (MTB oder H_6A) wurde spektrophotometrisch untersucht. Es wurde festgestellt, daß Eisen(III) und MTB zwei Komplexe der Zusammensetzung Eisen(III)-MTB = 1:1 und 1:2 bilden. Der 1:1-Komplex ist in saurem Medium mit Eisenüberschuß stabil, der 1:2-Komplex in schwach sauren oder alkalischen Medien mit überschüssigem MTB. Die Absorptionsmaxima liegen bei 610 nm (1:1) und 515 nm (1:2), die molaren Extinktionskoeffizienten sind $1{,}73 \pm 0{,}01 \cdot 10^4$ bzw. $3{,}21 \pm 0{,}05 \cdot 10^3$. Die Natur der beiden Komplexe bei pH 6 und die Stabilitätskonstanten wurden ermittelt:

$\log \beta_{11} = 20{,}56 \pm 0{,}07$, $\log \beta_{112} = 43{,}29 \pm 0{,}09$, $\log \beta_{12} = 6{,}66 \pm 0{,}05$.

Résumé—On a étudié par spectrophotométrie la réaction entre le fer (III) et le bleu de méthylthymol (MTB ou H_6A). On a établi que le fer (III) et le MTB forment deux complexes de compositions fer(III): MTB = 1:1 et 1:2. Le complexe 1:1 est stable en milieu acide contenant un excès de fer et le complexe 1:2 est stable en milieux légèrement acide ou alcalin contenant un excès de MTB. Les maximums d'absorption sont à 610 mμ (1:1) et 515 mμ (1:2), les coefficients d'absorption moléculaire étant $1{,}73 \pm 0{,}01 \times 10^4$ et $3{,}21 \pm 0{,}05 \times 10^3$ respectivement. On a déterminé la nature des deux complexes à pH 6 et les constantes de stabilité: $\beta_{11} = 20{,}56 \pm 0{,}07$, $\log \beta_{112} = 43{,}29 \pm 0{,}09$, $\log \beta_{12} = 6{,}66 \pm 0{,}05$.

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CATALYTIC MICRODETERMINATION OF CHROMIUM(VI)

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Summary—An automatic spectrophotometric kinetic method for the microdetermination of chromium(VI) is described, based on catalysis of the hydrogen peroxide–iodide reaction. The time required for the reaction to produce a small fixed amount of tri-iodide is measured automatically, and is proportional to the chromium(VI) concentration. Maximum tolerable amounts of various interfering ions were investigated. From 0·6 to 3·0 μg of chromium(VI) can be determined with relative errors of 1–2%, with measuring times of 10–50 sec.

THE phenomenon of catalysis has already been utilized for the determination of chromium.[1–3] In this paper, an automatic spectrophotometric reaction-rate method for the microdetermination of chromium is presented. The method utilizes the hydrogen peroxide–iodide reaction, which is catalysed by sexivalent chromium, and the type of automatic spectrophotometric reaction-rate system used for the determination of glucose and molybdenum.[4,5] The rate of appearance of tri-iodide is measured by following continuously the rate of change of the output voltage of a photoconductive circuit. The time required for the reaction to produce a small fixed amount of tri-iodide and therefore for the absorbance to increase by a preselected amount—as given by a preselected change of 1·00 mV in the output voltage of the photoconductive circuit—is measured automatically and related directly to the chromium concentration.

Speed, precision and simplicity are distinctive advantages of the automatic method. The sample is transferred into the reaction cell, sulphuric acid and iodide are added, hydrogen peroxide is injected to start the reaction, the starter pressed and the data read off a dial shortly after the start. Microamounts of chromium in the range 0·6–3·6 μg may be determined with relative errors of 1–2% and measurement times of only 10–50 sec.

The method was tested by determining the solubility of barium chromate and the values obtained agree closely with those reported in the literature.

The time interval required for the preselected change in output voltage depends not only on the chromium concentration but also on the pH, temperature, and the concentrations of iodide and hydrogen peroxide. By adjusting the conditions the reaction is made pseudo first-order with respect to chromium. At chromium(VI)-concentrations below $2 \times 10^{-5}M$ and at about pH 2 the rate of oxidation of iodide by chromium(VI) is negligible and therefore the chromium concentration of the samples should be brought into the range 0·15–1·2 ppm by appropriate dilution.

EXPERIMENTAL

Instrumentation

The same experimental set-up was used as for the determination of molybdenum.[5]

Reagents

All reagents were prepared in doubly distilled water from reagent-grade materials.

Sulphuric acid, 0·3*M*.

Potassium iodide, 0·07*M*.

Hydrogen peroxide, 0·018*M*. Prepared daily from the 30% solution.

Chromium standards. Dissolve 0·2829 g of potassium dichromate in 1 litre of water. This solution contains 100 ppm of chromium. Working chromium standards of 0·2, 0·6 and 1·0 ppm are prepared from the 100 ppm chromium solution by appropriate dilution.

All working standards, reagent solutions and samples were kept in a water-bath at 25 ± 0·05° during use.

Procedure

Preparation of equipment. Switch the Spectro-Electro titrator to the Spectro position at least 1 hr before the measurements are started, to ensure good stability from the light source. Dial the nominal 525 second-order interference filter on the filter wheel and place a Corning No. 5860 glass cut-off filter in the auxiliary holder: this setting provides a narrow transmittance band at 365 mμ. Throw the polarity switch to position 1. A few minutes before the measurements are started, turn the comparator unit to ON and the range selector switch to PNP ± 0·01 V.

Measurement step. Set the comparator Zero Adjust control at 5·30. Transfer by pipette 3·00 ml of sample or standard chromium solution into the reaction cell. Inject with suitable syringes 0·25 ml of sulphuric acid and 0·100 ml of potassium iodide into the cell. Throw the comparator reagent selector switch to position 1 to start the stirring and adjust the Spectro balance control so that the meter needle is at the centre. Set the comparator Zero Adjust at 4·50, and 1 min after the start of the stirring, inject 0·100 ml of hydrogen peroxide solution and press *at once* the start button on the model Q-RR reaction-rate adapter. The analysis is completed automatically and the number on the read-out dial is recorded. Repeat the procedure for each analysis.

RESULTS AND DISCUSSION

Basic considerations concerning contamination, temperature control, premeasurement times and preparation of working curves were similar to those previously reported.[6] Reasons for the choice of various features of the procedure and results of the analyses of aqueous chromium solutions are given below.

Choice of wavelength. Iodine can be detected and its rate of formation followed with starch or Variamine Blue. In the proposed method tri-iodide is used as its own indicator because of its high absorbance in the near ultraviolet. Although the tri-iodide has an absorption maximum at 353 mμ, a narrow band at about 365 mμ was selected because of greater instrument sensitivity.

Optimum concentration of reagents. The rates of both the catalysed and the uncatalysed reactions depend on the hydrogen peroxide concentration. Figure 1 illustrates the effect of hydrogen peroxide concentration on the rate of the reaction, all other conditions being as described under *Procedure*. In a study of the effect of hydrogen peroxide concentration on the rate of the uncatalysed reaction, the blank increased from 0·035 to 0·080 ppm of chromium as the hydrogen peroxide concentration in the final solution increased from 0·64 to $5{\cdot}1 \times 10^{-4}M$. A concentration of $5{\cdot}1 \times 10^{-4}M$ hydrogen peroxide was chosen because at smaller concentrations the precision was not as good.

Figure 2 illustrates the variation of reaction rate with sulphuric acid concentration, other conditions being the same as described under *Procedure*. Although measurement times decrease with increasing acid concentration a final sulphuric acid concentration of 0·022*M* was chosen because at higher acid concentrations the rate of oxidation of iodide by chromium(VI) becomes significant.

There is a linear relationship between reaction rate and iodide concentration, but

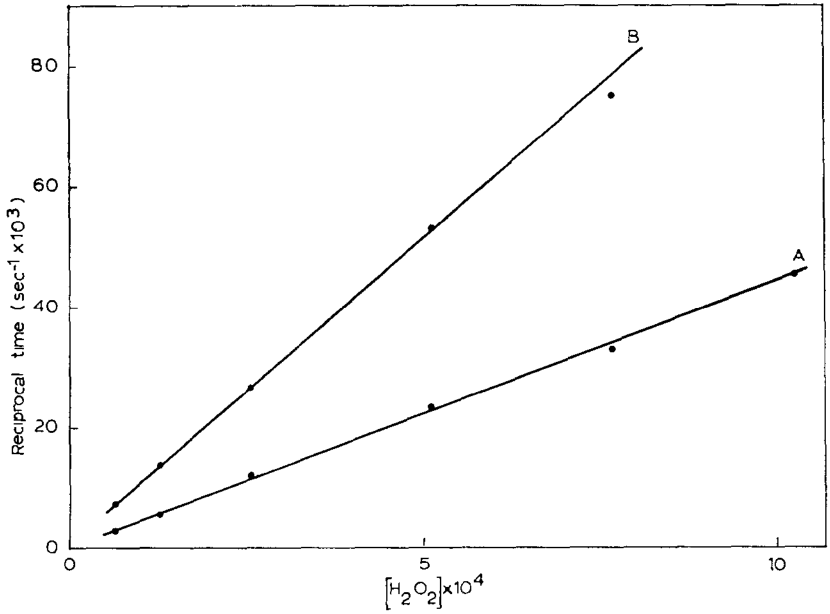

FIG. 1.—Relation between reaction rate and hydrogen peroxide concentration. A, 0·2 ppm Cr; B, 0·6 ppm Cr; other conditions as under procedure.

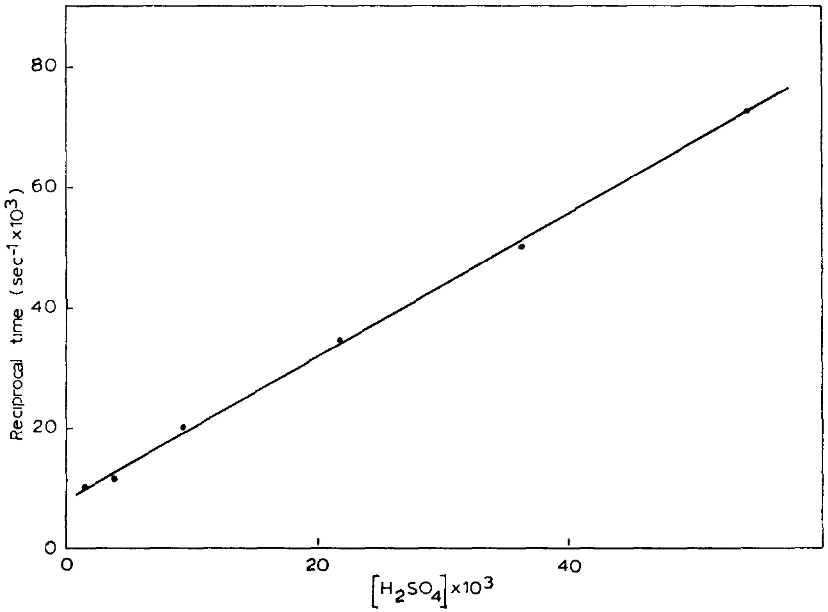

FIG. 2.—Dependence of the rate of the reaction on the sulphuric acid concentration. Cr 0·4 ppm; other conditions as under procedure.

the blank too increases as the iodide concentration increases. A 0·002*M* potassium iodide concentration was chosen as a compromise.

Effect of temperature. The working curves obtained at 20°, 30° and 35° are similar to those obtained at 25°. The blank increases as the temperature increases. The reaction has a relatively small temperature coefficient of about 2.5% at 25 ± 2°.

Quantitative data. Results for the determination of chromium in pure aqueous potassium dichromate solutions are given in Table I. The data indicate that chromium in the range 0·6–3·0 μg could be determined with relative errors of about 2%. Measurement times were the same when potassium chromate was substituted for the potassium dichromate. The abscissa intercept (blank) on the working curve is a function of the rate of the uncatalysed reaction and the contamination of the reagents with substances catalysing the hydrogen peroxide–iodide reaction. Under the conditions of the procedure the blank range over a period of several weeks was 0·05–0·08 ppm of chromium.

TABLE I.—RESULTS FOR AQUEOUS CHROMIUM SOLUTIONS

Reciprocal time, *sec*$^{-1}$ · 10^3	Chromium* in 3-ml sample, μg		Relative error, %
	Taken	Found†	
20·3	0·600	0·585	−2·5
28·0	0·900	0·900	—
43·7	1·500	1·530	+2·0
56·5	2·100	2·040	−2·9
73·7	2·700	2·730	+1·1

* Present as $Cr_2O_7^{2-}$.
† From straight-line working curve, average of two values.

To check the reproducibility of the proposed procedure ten replicate determinations were made at the 0·3-ppm chromium level; the relative standard deviation was 2·3%.

The solubility of barium chromate was determined by the proposed method and found to be 0·0034 g/l. at 16° (reported value in *Handbook of Chemistry and Physics* is 0·0035 g/l.).

Interferences. Reducing or oxidizing agents should be eliminated before the measurements are made. To investigate the effect of various ions that might interfere in the determination of chromium, the measurement step was modified as follows: after the addition of a chromium standard (0·3 ppm), 0·25 ml of water or of the solution of the ions being examined was injected into the reaction cell. Strongly alkaline solutions were neutralized with sulphuric acid before their effect on the reaction rate was studied. The following ions did not affect the rate of the reaction even when their concentrations were several thousand times that of the chromium: sodium, potassium, manganese(II), nickel, chloride and nitrate. Table II shows the effect of interfering ions. The large negative error caused in the presence of even small amounts of EDTA precludes its use as a masking agent for interfering ions.

Although iron(II) ions catalyse the hydrogen peroxide–iodide reaction (maximum tolerable ratio of Fe(II)/Cr(VI) is about 2·3 for a positive error of 5%) measurement times were increased when this ratio was in the range 0·5–2·0, probably because of reduction of chromium(VI) by iron(II).

TABLE II.—EFFECT OF VARIOUS IONS ON CHROMIUM DETERMINATION AT A CONCENTRATION OF $5{\cdot}77 \times 10^{-6}M$ (0·3 ppm)

Ion*	Source	Ratio of added ion concn. to chromium concn.	Ion†	Source	Ratio of added ion concn. to chromium concn.
$Mo_7O_{24}^{6-}$	$(NH_4)_6Mo_7O_{24}$	0·002	Ce^{4+}	$Ce(SO_4)_2$	0·2
WO_4^{2-}	Na_2WO_4	0·006	$PtCl_6^{2-}$	$(NH_4)_2PtCl_6$	0·6
VO^{2+}	$VOSO_4$	0·3	EDTA	Na-EDTA	3
$OsCl_6^{2-}$	$(NH_4)_2OsCl_6$	0·4	$H_2PO_4^-$	KH_2PO_4	350
HfO^{2+}	$HfOCl_2$	0·4	Mg^{2+}	$MgSO_4$	600
SeO_3^{2-}	H_2SeO_3	3	Co^{2+}	$CoCl_2$	2300
ZrO^{2+}	$ZrOCl_2$	3	F^-	KF	2400
$IrCl_6^{3-}$	$(NH_4)_3IrCl_6$	6	Zn^{2+}	$ZnCl_2$	3000
Fe^{3+}	$Fe(NO_3)_3$	10	NH_4^+	NH_4Cl	3000
Y^{3+}	$Y(NO_3)_3$	17			
UO_2^{2+}	$UO_2(NO_3)_2$	35			
Th^{4+}	$ThCl_4$	60			
ReO_4^-	$KReO_4$	100			
Cu^{2+}	$Cu(NO_3)_2$	120			

* These ions in the stated ratio caused a positive relative error of less than 5%.
† These ions in the stated ratio caused a negative relative error of less than 5%.

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Zusammenfassung—Es wird eine automatische spektrophotometrisch-kinetische Methode zur Mikrobestimmung von Chrom(VI) beschrieben, die auf der Katalyse der Reaktion zwischen Wasserstoffperoxid und Jodid beruht. Die Reaktionszeit bis zur Bildung einer kleinen vorgegebenen Menge Trijodid wird automatisch gemessen; sie ist der Chrom(VI)-Konzentration proportional. Die maximal zulässigen Mengen mehrerer störender Ionen wurden ermittelt. 0,6–3,0 μg Chrom(VI) wurden in Meßzeiten von 10–50 s mit relativen Fehlern von 1–2% bestimmt.

Résumé—On décrit une méthode spectrophotométrique cinétique automatique pour le microdosage du chrome(VI), basée sur la catalyse de la réaction eau oxygénée–iodure. Le temps nécessité par la réaction pour produire une petite quantité fixée de triiodure est mesuré automatiquement, et il est proportionnel à la concentration en chrome(VI). On a étudié les quantités maximales tolérables de divers ions gênants. On a dosé de 0,6 à 3,0 μg de chrome(VI) avec des erreurs relatives de 1–2%, avec des temps de mesure de 10–50 s.

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RADIOCHEMISCHE TRENNUNGEN MIT HILFE DER RINGOFENMETHODE—III. DIE SYSTEME ^{90}Sr/^{90}Y UND ^{140}Ba/^{140}La

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Zusammenfassung—Mit Hilfe der Ringofenmethode lassen sich auf Rundfiltern aus Carboxymethyl-Cellulose ^{90}Y von ^{90}Sr und ^{140}La von ^{140}Ba schnell abtrennen. Die höchsten Ausbeuten ($>99\%$ ^{90}Y bzw. 85–95% ^{140}La) und Dekontaminationsfaktoren (5×10^3–10^4 bei ^{90}Y bzw. 10^3 bei ^{140}La) erreicht man unter Verwendung von ÄDTA als Komplexbildner und Wasser als Waschflüssigkeit. Die Halbwertszeiten der im Ring konzentrierten Tochternuklide ^{90}Y und ^{140}La wurden zu 64,7 ± 0,3 h bzw. 40,5 ± 0,2 h bestimmt. Mit einer 1%igen α-Hydroxy-i-buttersäure-Lösung vom pH 4,8 als Waschflüssigkeit läßt sich aus einem ^{90}Sr/^{90}Y—^{140}Ba/^{140}La-Gemisch ^{90}Y selektiv mit 85–90% Ausbeute abtrennen.

Die Ringofenmethode nach Weisz läßt sich vorteilhaft für einfach und schnell auszuführende radiochemische Trennungen heranziehen, wie kürzlich an den Mutter-Tochter-Paaren ^{137}Cs/^{137m}Ba und ^{99}Mo/^{99m}Tc gezeigt werden konnte.[1,2] Im folgenden wird beschrieben, wie sich dieses Verfahren auch auf die Systeme ^{90}Sr/^{90}Y und ^{140}Ba/^{140}La ausdehnen läßt, wobei die Mutternuklide wiederum im Zentrum von Rundfiltern fixiert bleiben, während die Töchter "abgemolken" und in scharfen Ringzonen von 22 mm Durchmesser konzentriert werden. Hierbei gelangen Ionenaustauschpapiere aus substituierter Cellulose zur Anwendung und nicht, wie in den beiden oben zitierten Arbeiten, mit anorganischen Ionenaustauschern imprägnierte Rundfilter.

Verfahren zur Trennung von ^{90}Sr und ^{90}Y auf Ionenaustauschersäulen wurden bereits des öfteren beschrieben. T. Ogura, T. Tarutani und S. Misumi[3] verwenden einen mit Hydrogencarbonat beladenen Anionenaustauscher. L. Klerkx[4] arbeitet mit einem Anionenaustauscher in der Oxalatform. In diesen Fällen wird ^{90}Sr vor ^{90}Y eluiert.

Den umgekehrten Fall—Fixieren von ^{90}Sr auf der Säule—realisieren M. Ziegler und W. Rittner[5] durch Verwendung von Anionenaustauschersulfaten. Sehr reine ^{90}Y-Präparate erhalten F. Maćäsek und R. Čech,[6] indem sie das Nuklid mit 0,01 m ÄDTA-Lösung von der Mutter ^{90}Sr "abmelken", welche auf einem Kationenaustauscher (NH_4^+-Form) festgehalten wird. Für die "Melk"-Systeme ^{90}Sr/^{90}Y und ^{140}Ba/^{140}La beschreiben K. H. Lieser und K. Bächmann[7] ähnliche Verfahren mit Milchsäure als Komplexbildner. ^{90}Sr-^{90}Y-Trennungen durch Chromatographie auf Ionenaustauschpapieren führt P. C. Stein[8] aus, wobei je nach Bedingungen (Papiersorte, Komplexbildner) ^{90}Sr oder ^{90}Y am Startfleck zurückbleiben. Ähnliche Versuche zur chromatographischen Trennung von Uranspaltprodukten (u.a. ^{90}Sr/^{90}Y und

^{140}Ba/^{140}La) auf Cellulosephosphat mit verschiedenen Laufmitteln (u.a. α-Hydroxyisobuttersäure als Komplexbildner) beschreiben N. Getoff und H. Bildstein.[9] E. Cerrai und G. Ghersini[10] arbeiten auf Papieren, welche mit Di-(2-äthylhexyl-)orthophosphorsäure imprägniert sind. R. Kuroda und K. Oguma[11] trennen ^{90}Sr und ^{90}Y durch Isotopenaustausch-Chromatographie auf dünnen Schichten aus einer Mischung von Strontiumsulfat und Silicagel. H. Sorantin berichtete über Trennungen von ^{140}Ba und ^{140}La[12] sowie von ^{90}Sr und ^{90}Y[13] mit Hilfe des Ringofens: Beim Waschen mit 0,1–0,2n Ammoniumthiocyanatlösung wanderte jeweils das Mutternuklid in die Ringzone, während ^{140}La bzw. ^{90}Y im Zentrum des Rundfilters zurückblieben.

Eine Umkehrung dieser Verhältnisse gelang durch Verwendung verdünnter Schwefelsäure oder einer benzolischen Lösung von Thenoyltrifluoraceton als Waschflüssigkeit. Die Brauchbarkeit dieser Trennungen wurde dabei nur an Hand von Autoradiogrammen belegt, ohne Angaben über Ausbeute und Reinheit der abgetrennten Tochternuklide.

Die in der vorliegenden Arbeit beschriebenen Versuche zeigen, daß bei Verwendung von Rundfiltern aus Carboxymethyl-Cellulose ^{90}Y und ^{140}La mit befriedigender Reinheit und Ausbeute von ihren Mutternukliden abgetrennt werden können.

Filtermaterial sowie Reagens- und Waschlösungen

Selbstgeschnittene Rundfilter (5,5 cm Durchmesser) aus Carboxymethyl-Cellulose CM 82 der Fa. Whatman.

Wäßrige α-Hydroxy-i-buttersäure-Lösung (1%ig), mit 25%igem Ammoniak auf pH ~4,8 eingestellt.

Wäßrige Lösung von Arsenazo III (0,1%ig).

Wäßrige ÄDTA-Lösung (0,5%ig).

Radionuklidlösungen

Salpetersaure (0,05n) ^{90}Sr/^{90}Y-Lösung mit 2 μg Sr^{2+} pro ml als Träger; spez. Aktivität ~84 μC/ml.

Verd. salzsaure ^{140}Ba/^{140}La-Lösung mit 10 μg Ba^{2+} pro ml als Träger; spez. Aktivität ~13 μC/ml.

Messgeräte

Zählgerät FH 49 der Firma Frieseke u. Hoepfner, Erlangen-Bruck, mit Endfensterzählrohr FHZ 15 a.

ESONE-Meßplatz mit Einkanaldiskriminator der Firma Prof. Berthold, Wildbad; NaJ (Tl)-Kristall FH 421/Z 4 (Frieseke und Hoepfner).

100 Kanal-Impulshöhenanalysator Gammascope II der Firma Technical Measurement Corp., North Haven; Harshaw-NaJ (Tl)-Kristall (2″ × 2″; 8 S 8/EP).

DURCHFÜHRUNG DER TRENNUNGEN

^{90}Sr/^{90}Y

Es wurde 1 μl der ^{90}Sr/^{90}Y-Lösung auf die Mitte eines CM-Rundfilters aufgetragen, der Fleck getrocknet und das ^{90}Y in der üblichen Weise auf einem Ringofen (Temperatur ~125°) mit *ca.* 120 μl der α-Hydroxy-i-buttersäure- bzw. Arsenazo III-Lösung in die Ringzone gewaschen. Eine weitere Variante bestand in folgender Arbeitsweise: Nach dem Aufbringen der Radionuklidlösung auf das Rundfilter wurde mit 5 μl der ÄDTA-Lösung nachgetüpfelt und ohne zu trocknen mit etwa 120 μl dest. Wasser zum Ring gewaschen.

Nach der Trennung wurde das Rundfilter getrocknet und aus dem Zentrum desselben ein Scheibchen von 17 mm Durchmesser (mit dem Sr-Fleck in der Mitte) herausgeschnitten (vgl.[1]). Das Scheibchen (^{90}Sr) und das restliche Filter mit dem im Ring konzentrierten ^{90}Y gelangten anschließend zur β-Messung mit dem Endfensterzählrohr. Hierbei konnte durch Abdecken der Meßpräparate mit Aluminium (215 mg/cm^2) die ^{90}Y-Ausbeute im Ring ermittelt werden. Nachdem der Abfall des abgetrennten ^{90}Y über rund 10 Halbwertszeiten verfolgt worden war, wurde durch β-Messung von 17-mm Scheibchen und Ring (etwa 30 Tage nach der Trennung) der Dekontaminationsfaktor bestimmt. Nach Wiedereinstellung des radioaktiven Gleichgewichts wurde aus dem 17-mm Scheibchen (^{90}Sr/^{90}Y) erneut ^{90}Y abgemolken. Das Scheibchen wurde auf dem Ringofen auf die Mitte eines neuen CM-Rundfilters gepreßt[1,14] und das Tochternuklid mit 200–300 μl der α-Hydroxy-i-buttersäure- bzw.

Arsenazo III-Lösung in der Ringzone konzentriert. Analog zur oben beschriebenen Arbeitstechnik wurde auch folgender Weg beschritten: Das Filterscheibchen wurde mit 10 μl der ÄDTA-Lösung durchfeuchtet, getrocknet, auf die Mitte eines neuen CM-Rundfilters gepreßt und mit 150–200 μl dest. Wasser eluiert. Nach der Trennung wurde aus dem Zentrum des unteren Rundfilters ein Scheibchen von 18 mm Durchmesser ausgeschnitten, um störende ^{90}Sr-Aktivität zu entfernen (vgl.[1,2]). Die Messungen erfolgten wie oben beschrieben.

^{140}Ba/^{140}La

Nach Auftragen von jeweils 3 × 5 μl der ^{140}Ba/^{140}La-Lösung auf die CM-Rundfilter (nach je 5 μl trocknen), wurden die Trennversuche mit den gleichen Waschflüssigkeiten und in der gleichen Weise durchgeführt wie bei ^{90}Sr/^{90}Y.

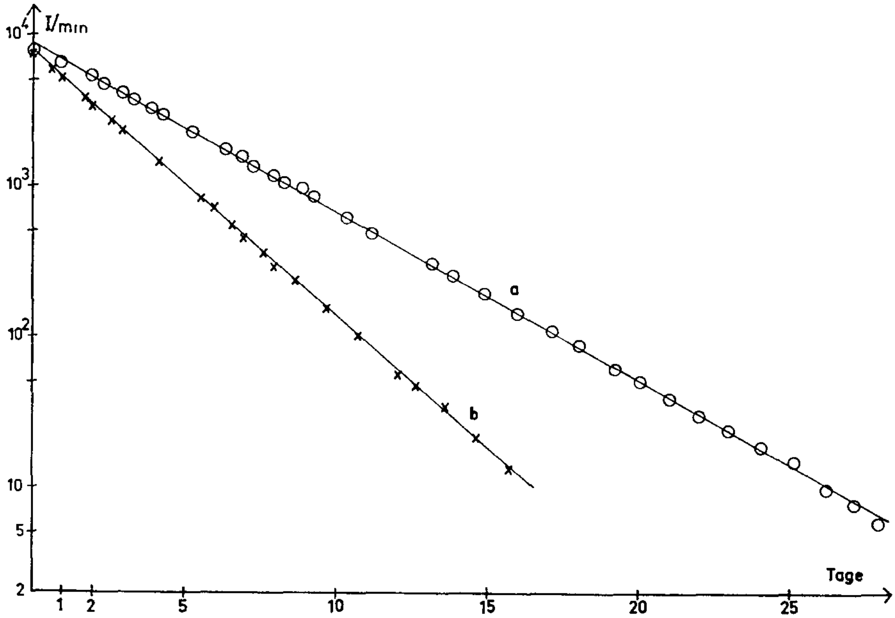

ABB. 1.—(*a*) Abfall von ^{90}Y im Ring (○)
(*b*) Abfall von ^{140}La im Ring (×).

Die ^{140}La-Ausbeute im Ring konnte an Hand des 1,6 MeV-γ-Peaks, der Dekontaminationsfaktor durch β-Messung (>20 Tage nach der Trennung) oder mit Hilfe des 0,16 MeV-Peaks von ^{140}Ba (15–20 Tage nach der Trennung) ermittelt werden. Der Abfall des im Ring konzentrierten ^{140}La wurde ebenfalls über rund 10 Halbwertszeiten verfolgt, und zwar durch β-Messung oder durch γ-Messung bei 1,6 MeV. 15–20 Tage nach der ersten Trennung wurden Abmelkversuche durchgeführt wie bei ^{90}Sr/^{90}Y beschrieben.

ERGEBNISSE UND DISKUSSION

Von den untersuchten Trennmöglichkeiten erwies sich diejenige mit ÄDTA als Komplexbildner und Wasser als Waschflüssigkeit für das Mutter-Tochter-Paar ^{90}Sr/^{90}Y als am besten geeignet. Es konnten hiermit ^{90}Y-Ausbeuten von >99 % und Dekontaminationsfaktoren von 5 × 10^3–10^4 erzielt werden. Dadurch wäre es beispielsweise möglich, mit diesem Verfahren ^{89}Sr-^{90}Sr/^{90}Y-Gemische schnell zu analysieren.

Abbildung 1*a* zeigt den Abfall von ^{90}Y im Ring. Aus vier solchen Geraden wurde durch Ausgleichsrechnung die Halbwertszeit des Nuklids zu 64,7 ± 0,3 h ermittelt.*

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* Die numerischen Rechnungen wurden an der Rechenanlage Siemens 2002 des Rechenzentrums der Universität Freiburg durchgeführt. Herrn Dr. J. Strähle, Lehrstuhl für Anorganische Chemie der Universität Freiburg, sei an dieser Stelle für die Ausarbeitung eines ALGOL-Programms gedankt.

Auch im System ^{140}Ba/^{140}La zeigte es sich, daß mit ÄDTA als Komplexbildner und Wasser als Waschflüssigkeit die besten Trennungen erreicht werden können. Die ^{140}La-Ausbeuten lagen zwischen 85 und 95 %, die Dekontaminationsfaktoren bei 10^3. Der ^{140}La-Abfall im Ring ist in Abb. 1*b* dargestellt. Aus sechs solchen Abfällen wurde die Halbwertszeit von ^{140}La zu 40,5 ± 0,2 h berechnet.* Abbildung 2 zeigt das

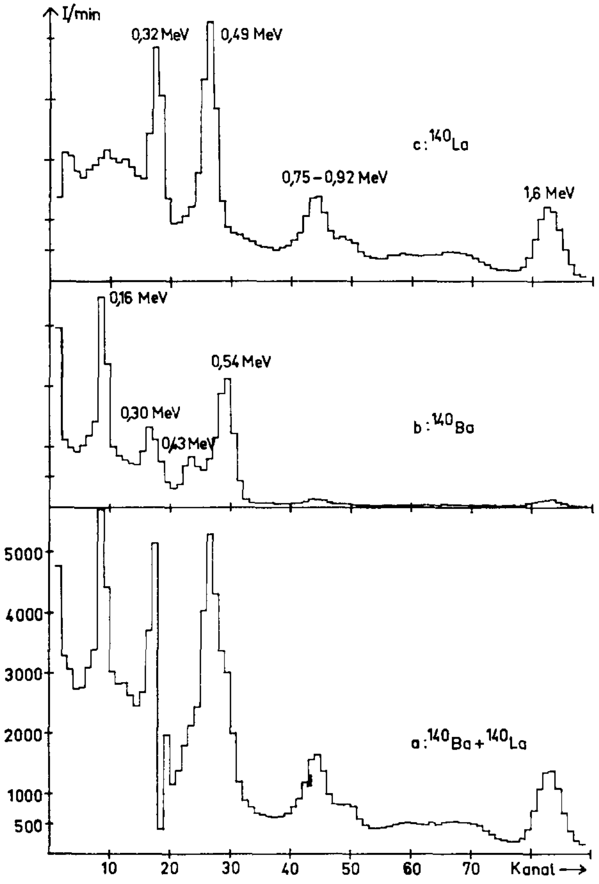

ABB. 2.—Spectren von (*a*) ^{140}Ba + ^{140}La vor der Trennung
(*b*) ^{140}Ba im 17-mm Scheibchen
(*c*) ^{140}La im Ring.

γ-Spektrum von ^{140}Ba/^{140}La vor der Trennung sowie die Spektren von 17-mm Scheibchen (^{140}Ba) und Ring (^{140}La) unmittelbar nach der Trennung.

Der bemerkenswerteste Unterschied im Verhalten der Systeme ^{90}Sr/^{90}Y und ^{140}Ba/^{140}La gegenüber den untersuchten Waschflüssigkeiten besteht darin, daß bei Verwendung der α-Hydroxy-i-buttersäure-Lösung ^{90}Y mit guter Ausbeute in die Ringzone wandert, ^{140}La jedoch fast vollständig beim ^{140}Ba im Zentrum des CM-Rundfilters zurückbleibt. Diese Tatsache kann man sich zunutze machen, um ^{90}Sr/^{90}Y neben ^{140}Ba/^{140}La zu bestimmen. In einem entsprechenden Versuch mit einem Gemisch der beiden Nuklidpaare (1 μl ^{90}Sr/^{90}Y-Lösung + 4 × 5 μl ^{140}Ba/^{140}La-Lösung) konnten 85–90 % des ^{90}Y mit der α-Hydroxy-i-buttersäure-Lösung im Ring konzentriert werden, während nur jeweils 0,2 % vom ^{90}Sr und ^{140}La mitwanderten. ^{140}Ba ließ sich nicht im Ring nachweisen.

Die geschilderten Untersuchungen sollten erneut die Leistungsfähigkeit der Ringofenmethode bei radiochemischen Trennungen demonstrieren. Die Verfahren dürften sowohl für radiochemisch-analytische Probleme als auch für Unterrichtszwecke geeignet sein.

Der Verfasser dankt Herrn Prof. Dr. W. Seelmann-Eggebert, dem Direktor des Institutes für Radiochemie im Kernforschungszentrum Karlsruhe, für die Überlassung von ^{140}Ba/^{140}La- Lösungen.

Summary—Rapid separations of ^{90}Y from ^{90}Sr and of ^{140}La from ^{140}Ba on carboxymethylcellulose filter papers by the ring-oven technique are described. Highest yields (>99 % for ^{90}Y and ∼90 % for ^{140}La) and decontamination factors ($5 \times 10^3 - 10^4$ for ^{90}Y and 10^3 for ^{140}La) are obtained by using EDTA as complexing agent and water for washing. The half-lives of the daughter-nuclides were found to be 64·7 ± 0·3 hr and 40·5 ± 0·2 hr for ^{90}Y and for ^{140}La respectively. ^{90}Y can be selectively separated with 85–90 % efficiency from a mixture of all four nuclides by using a 1 % solution of hydroxyisobutyric acid at pH 4·8 as eluent.

Résumé—On décrit des séparations rapides de ^{90}Y de ^{90}Sr et de ^{140}La de ^{140}Ba sur papiers filtres de carboxyméthylcellulose par la technique du four annulaire. On obtient les rendements (>99 % pour ^{90}Y et 90 % pour ^{140}La) et les facteurs de décontamination les plus élevés (5×10^3–10^4 pour ^{90}Y et 10^3 pour ^{140}La) par emploi d'EDTA comme agent complexant et d'eau pour le lavage. On a trouvé que les demi-vies des nucléides-filles sont de 64,7 ± 0,3 h et 40,5 ± 0,2 h pour ^{90}Y et ^{140}La respectivement. On peut séparer sélectivement ^{90}Y avec une efficacité de 85–90 % à partir d'un mélange des quatre nucléides en utilisant comme éluant une solution à 1 % d'acide hydroxyisobutyrique à pH 4,8.

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SIMPLE AND RAPID DETERMINATION OF MERCURY IN URINE AND TISSUES BY ISOTOPE EXCHANGE

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Summary—The method eliminates oxidation of organic material. Tracer quantities of ^{203}Hg are added to the sample and equilibrated with the stable mercury. ^{200}Hg vapor in nitrogen is passed through the sample in the presence of cysteine and at pH 7.4, and exchanges with the ^{203}Hg. The vapor is collected in a tube of activated Hopcalite placed in a gamma-counter. The increasing activity is recorded and the half-time of exchange is directly proportional to the mercury concentration in the sample. The method is best suited for urine samples containing more than 10 μg Hg/l.

CURRENT methods for the determination of mercury in urine and other biological materials require that the organic material should be removed by chemical oxidation, either partially or completely. As has been stressed by others,[1,2] the chief problem lies in the digestion procedure. Too vigorous oxidation results in losses of mercury by volatilization, too little leads to incomplete extraction by the complexing agents (*e.g.*, dithizone). If the chemical oxidant is not completely reduced after the digestion procedure other complications result.

The method described here avoids these difficulties by making use of an entirely new procedure. Sufficient quantities of cysteine are added to the biological sample to complex all the mercury present. Trace quantities of radioactive mercury, ^{203}Hg, are added, and immediately equilibrate with the non-active mercury in the cysteine complex. The biological sample, now containing labelled mercury complexed to cysteine, is exposed to non-radioactive mercury vapor. A rapid isotopic exchange takes place resulting in the transfer of radioactivity to the vapor phase. Experimental conditions are adjusted so that the half-time of the exchange process is directly proportional to the concentration of mercury in the sample.

The isotope exchange reaction was first applied by Clarkson, Rothstein and Sutherland[3] to the determination of the rate of cleavage of mercury from organic mercurial diuretics in body tissues, and subsequently used by Magos[4] for the measurement of mercury concentrations in air.

THEORETICAL

Solutions of various salts of mercury are capable of undergoing isotopic exchange with mercury vapor in contact with the solution[3]. As the non-active vapor passes through the exchange vessel, it acquires radioactivity by isotope exchange with the radioactive mercury in the aqueous phase. The rate of loss of radioactivity from the solution is given by the equation

$$\frac{-d[^{203}\mathrm{Hg}_{\mathrm{aq}}] \,.\, V}{dt} = \frac{a \,.\, [^{203}\mathrm{Hg}_{\mathrm{V}}]}{[^{200}\mathrm{Hg}_{\mathrm{V}}]} \tag{1}$$

where V ml is the volume of the aqueous phase, $[^{203}\mathrm{Hg}_{\mathrm{aq}}]$ and $[^{203}\mathrm{Hg}_{\mathrm{V}}]$ are the activities (in counts.min^{-1-}.ml^{-1}) of the aqueous and vapor phases respectively, $[^{200}\mathrm{Hg}_{\mathrm{V}}]$ is the chemical concentration of mercury in the vapor phase (in μg/ml), and a is the vapor flow rate in μg/min. If the vapor achieves complete isotopic equilibrium with the solution, the specific activity of the vapor leaving the exchange vessel will be equal to the specific activity of the mercury in the aqueous phase and equation (1) becomes

$$-d[^{203}\mathrm{Hg}_{\mathrm{aq}}] \,.\, V = \frac{a \,.\, [^{203}\mathrm{Hg}_{\mathrm{aq}}]\, dt}{[^{200}\mathrm{Hg}_{\mathrm{aq}}]} \tag{2}$$

where $[^{200}\mathrm{Hg}_{\mathrm{aq}}]$ is the concentration of mercury in the aqueous phase, in μg/ml. Provided that V, a and $[^{200}\mathrm{Hg}_{\mathrm{aq}}]$ remain constant throughout the exchange process, equation (2) may be integrated to give

$$-\ln \frac{[^{203}\mathrm{Hg}_{\mathrm{aq}}]_t}{[^{203}\mathrm{Hg}_{\mathrm{aq}}]_o} = \frac{at}{[^{200}\mathrm{Hg}_{\mathrm{aq}}] \,.\, V} \tag{3}$$

where the subscripts o and t refer to zero time and time t respectively. Equation (3) states that the rate of loss of radioactivity will be first-order and the time for the loss of half the total activity from the aqueous phase, $t_{1/2}$, will be given by

$$t_{1/2} = 0{\cdot}690 \,.\, \frac{V[^{200}\mathrm{Hg}_{\mathrm{aq}}]}{a} \tag{4}$$

In other words the half-time will be directly proportional to the concentration of mercury in the aqueous phase. The slope of the line may be calculated from the known values of V and a.

EXPERIMENTAL

Reagents

Cysteine hydrochloride. Sodium hydroxide, 1·0*M*. Sodium chloride, 0·9% solution. Octyl alcohol. ^{203}Hg isotope supplied as mercuric nitrate at a specific activity of approximately 1 mc/mg (Cambridge Nuclear Co., Cambridge, Mass.).

Apparatus

The general arrangement of the apparatus is shown schematically in Fig. 1. Mercury vapor was generated by passing nitrogen at a flow-rate of 240 ml/min through a midget impinger (Gelman Instrument Co., Ann Arbor, Mich. Model No. 7202) containing a small quantity of metallic mercury. The impinger was immersed in water at 45°. The vapor was passed through a second impinger containing a similar amount of metallic mercury but maintained at room temperature. The nitrogen gas emerging from the second impinger contained almost the saturation level of mercury (20 mg/m^3). The vapor then passed to the exchange vessel where it bubbled through the aqueous phase containing the radioactive mercury. The vessel consisted of a vertical pyrex glass tube, length 52·5 cm, internal diameter 1·9 cm, stoppered at each end by rubber bungs (Fig. 2) and had a nylon inlet-tube (Labtician Products, Hollis, New York, 0·096 in. bore, 0·125 in. outside diameter) extending to the bottom, the lower end of the nylon tube being heat-sealed and perforated with small holes. A short nylon outlet-tube passed through the upper rubber stopper. The issuing vapor was passed through a water-trap consisting of a small disposable plastic test-tube, 12 × 75 mm (Falcon Plastics, California) and then through a similar tube containing about a 1-in. length of activated Hopcalite. The hopcalite tube was placed in an NaI well-crystal to record ^{203}Hg activity. The counting equipment consisted of a decade counter (Radiation Instrument Detection Laboratories, Des Plaines, Ill., Model No. 49–51),

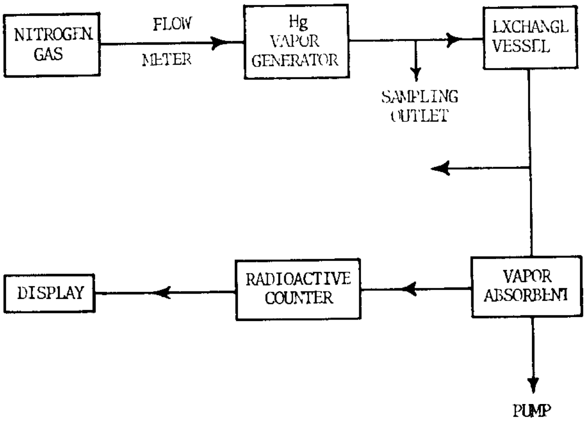


FIG. 1.—Schematic arrangement of apparatus.

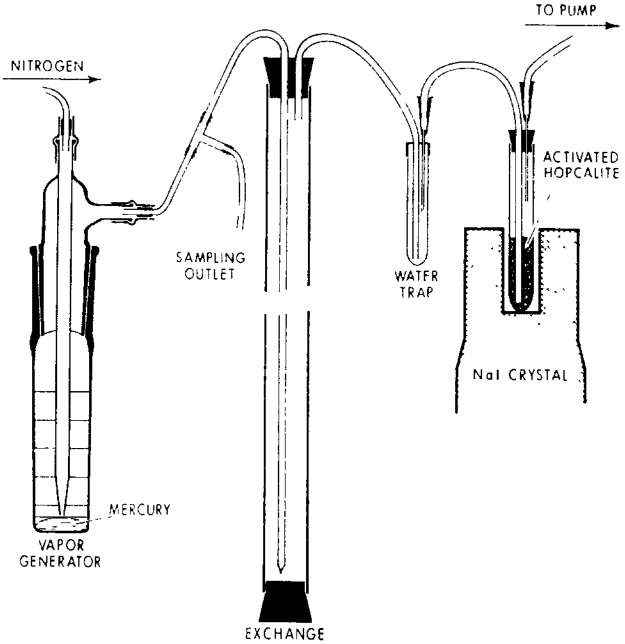


FIG. 2.—The exchange and counting assembly.

a rate-meter (Packard Inst., Co., La Grange, Ill., Model No. 280 A) and a pen-recorder (Leeds Northrup, Philadelphia, Pa. Type G.). Nitrogen gas was drawn through the system by a small electric pump (Universal Electric C., Owosso, Mich., Model No. 3) and the flow-rate recorded by a flow-meter (Brock Inst. Co., Hatfield, Pa.).

Procedure

Pour 70 ml of urine into a 100-ml graduated cylinder containing 3·15 g of cysteine hydrochloride and 22·5 ml of 1·0*M* sodium hydroxide. Add a trace quantity of ^{203}Hg isotope to give at least 10000 cpm and a final mercury concentration of $10^{-8}M$. Dilute to the 100-ml mark with 0·9% sodium chloride solution and add 1 ml of octyl alcohol to prevent foaming. Mix the contents of the cylinder and pour them directly into the exchange vessel. Start the nitrogen flow (containing mercury vapor at 17 mg/m^3) at a rate of 240 ml/min. Record the radioactivity in the hopcalite absorbent as a function

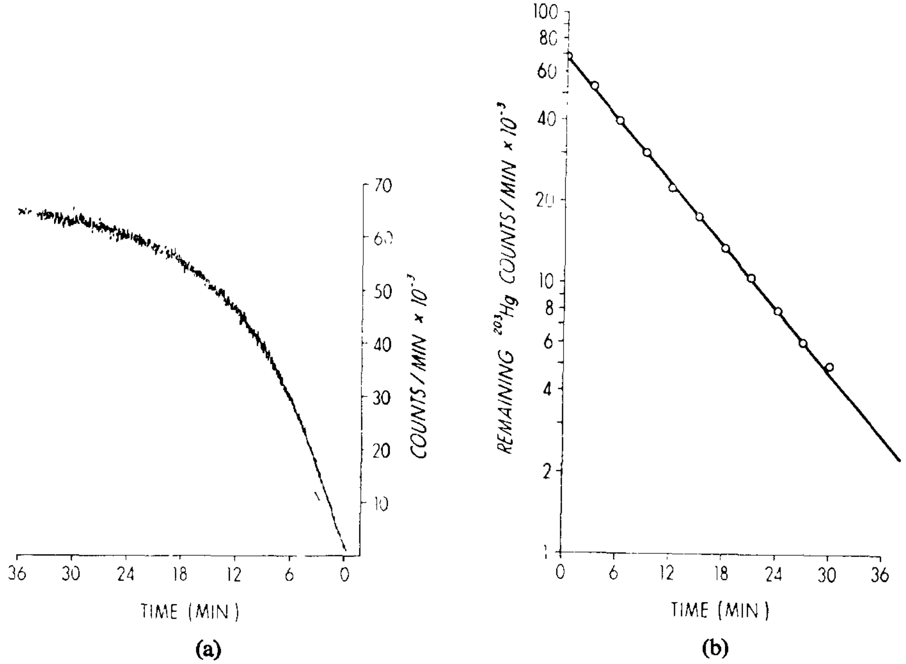


FIG. 3.—(*a*) Recorder tracing. (*b*) Semi-log plot.
The radioactivity remaining in the solution at any time was calculated from the pen-recording as described in the text.

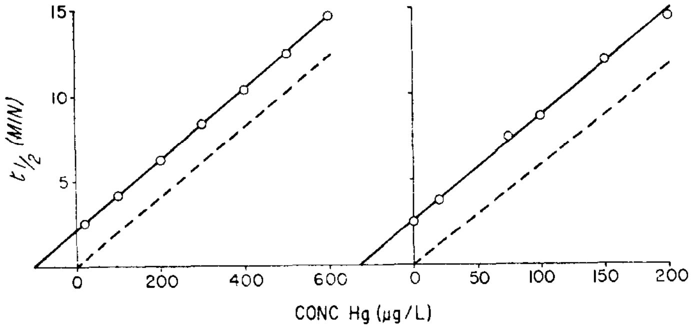
of time and stop the exchange run when the activity in the hopcalite has become steady. At this point all the radioactivity in the exchange vessel is completely transferred to the hopcalite, so the final trace on the recorder represents the initial radioactivity in the urine, and the difference between the final pen-recording and the pen-recording at any given time during the exchange run is the amount of activity remaining in the urine. This value is plotted on semi-log paper (Fig. 3) against time and yields a straight line from which the half-time can be calculated. The amount of mercury originally present in the urine sample is calculated from the half-time by referring to the standard curve.

To measure the mercury in kidney or liver, 1 g wet-weight of tissue is chopped and homogenized in 0·9% sodium chloride solution with a tissue grinder, made up to a volume of 70 ml with 0·9% sodium chloride solution, and then treated identically to the urine sample.

Prepare a standard curve by applying the procedure to 0·9% sodium chloride solutions containing known amounts of mercury(II) chloride covering the mercury concentration range 10^{-7}–$3 \times 10^{-6}M$ and plot $t_{1/2}$ against the concentration of mercury added.

RESULTS

Two typical standard curves are shown in Fig. 4. In both cases the slope of the line deviates only slighly from that calculated from equation (4), indicating that isotopic exchange is close to 100%. Figure 4*a* covers the range of mercury concentration most frequently found in people having a low to medium exposure to mercury.[8] To measure the low concentration of mercury in normal urine samples, the mercury concentration in the vapor should be reduced from 17 to approximately 5 mg Hg/m^3, to obtain a curve as shown in Fig. 4*b*. The intercept on the abscissae in both standard curves represents a blank reading due to mercury present in the standards in excess of that which was added. Part of the blank represents impurity in the reagents. The fact that the intercept was greater at the higher mercury vapor concentration (Fig. 4*a*, 65 μg/l.: Fig. 4*b*; 45 μg/l) indicates that part of the blank was due to mercury vapor which had dissolved in the solution in the exchange vessel.



(a) (b)

FIG. 4.—(*a*) Standard curve obtained with a vapor concentration of 17 mg Hg/m³. (*b*) Standard curve used for low concentrations of mercury with a vapor concentration of 5 mg Hg/m³.

The exchange half-times, $t_{1/2}$, calculated from the semi-log plot of Fig. 3 were plotted against the concentration of mercury in standard solutions. The broken lines are the theoretical relationship calculated according to equation (4) in the text.

TABLE I.—RECOVERY OF MERCURY ADDED *in vitro* TO HUMAN URINE

Number of samples	Mercury added ^{200}Hg µg/l	^{203}Hg	Mercury found ^{200}Hg + ^{203}Hg µg/l	Standard deviation µg/l	Net difference µg/l	Recovery %
5	0	0·025	13	1·4	13	—
5	100	0·025	110	2·6	10	97
5	200	0·025	207	1·1	7	97
5	300	20	340	2·8	20	102
5	400	10	418	1·9	8	99

Reducing the vapor tension, as predicted by equation (4), increases the slope of the standard curve so that lower concentrations of mercury give exchange half-times which can be measured accurately. The mercury vapor concentrations were measured with a "Kitagawa" detector (Union Industrial Equipment Corp., Fall River, Mass.).

When known amounts of mercury(II) chloride were added to urine samples, the mean recoveries for each group of 5 urines were between 97 and 102%, Table I. The urines were from laboratory workers with no history of mercury exposure. The mean differences between the mercury added and found varied from 7 to 20 µg/l. These values lie in the reported normal range[6] of 10–50 µg/l.

Similarly complete recovery of mercury was obtained when the metal was given to rats and the urine was subsequently analyzed, Table II. The mercury concentration in the urine was measured by counting a 1-ml sample (column 1, Table II), then an exchange run was made (column 2, Table II). The two sets of results agree well.

To check that mercury added *in vitro* to the urine equilibrated with the mercury already present, a small amount of mercury (II) chloride labelled with the ^{203}Hg isotope was added. The exchange half-time was measured and the mercury concentration calculated from it (column 3, Table II) was found to be equal to the sum of the *in vivo* and *in vitro* mercury, indicating that complete equilibration had taken place.

The complete recoveries obtained when mercury(II) chloride is added *in vitro* or *in vivo* to urine indicate that the basic assumptions of the procedure are correct, *viz.*, that the tracer mercury ^{203}Hg equilibrates rapidly with non-radioactive mercury

TABLE II.—DETERMINATION OF MERCURY IN URINE AND TISSUE HOMOGENATES FROM RATS INJECTED WITH MERCURY(II) CHLORIDE LABELLED WITH ^{203}Hg

Sample		Mercury μg/l		
		Counting*	Exchange†	Exchange after *in vitro* addition‡
Urine				
	(1)	222·5	222	236
	(2)	424	435	535
	(3)	55	43	60
Homogenates				
Kidney	(1)	764	780	795
	(2)	835	880	892
Liver	(1)	330	340	358

* Calculated from activity in sample.

† Calculated from exchange half-time.

‡ Addition of 14 μg of Hg per l. to urine and homogenate samples (added as $HgCl_2$ labelled with ^{203}Hg).

originally present in the sample, that all the mercury in urine is converted into its cysteine complex, and that the mercury in the complex undergoes complete isotopic exchange with the vapor.

DISCUSSION

Flow of mercury vapor and carrier gas

As indicated by equation (4) and confirmed by experiment, the exchange half-time is inversely proportional to the vapor flow-rate. This fact allows the exchange half-time to be set for any given value of the mercury concentration. When dealing with low concentrations of mercury, it is convenient to reduce the mercury vapor concentration so that the half-time falls within the response time of the recording equipment and yet is not too large to make the measurement very time-consuming.

Nitrogen was used as the carrier gas in order to remove oxygen from the system. There were three reasons for this: to prevent formation of any oxide layer over the metallic mercury in the vapor generator; to prevent any oxidation of cysteine in the exchange vessel; to avoid any conversion of mercury vapor into mercury(II) ions in the aqueous phase, which is known to require oxygen.[7]

In principle it is best to make the flow of nitrogen as rapid as possible so that the transit time of mercury in the plastic tubing is brief. In practice the flow is limited by the rate at which bubbles will pass through the exchanger without spillage or excessive foaming. A flow of 240 ml/min is close to the practical maximum and this requires the use of an antifoaming agent when biological samples are being analyzed.

Cysteine, 0·2*M*, *pH* 7·4

In order to measure non-radioactive mercury present in biological samples two conditions had to be met: first, that the non-radioactive mercury would immediately equilibrate with trace quantities of ^{203}Hg isotope added to the sample, and second that the total mercury in the labelled sample should be converted into one chemical species capable of undergoing rapid isotope exchange with mercury vapor. The use of the monothiol compound cysteine achieved both conditions. This compound was chosen because it had previously been shown that mercury complexed with cysteine underwent rapid isotopic exchange with mercury vapor[3] and that concentrations of monothiol compounds greater than $10^{-2}M$ were capable of removing mercury from tissue homogenates:[8] other monothiol compounds may also be used, but cysteine is the cheapest and most readily available commercially.

The pH of 7·4 was used because the reaction is not sensitive to small fluctuations in pH in this region. The exchange rate is reduced in acidic solutions of cysteine, and, on the other hand, cysteine is readily oxidized at very high pH values.

Antifoaming agents

These are necessary to prevent excessive foaming when urine and tissue homogenates are present in the exchange vessel. However, octyl alcohol reduces the exchange rate. Complete isotopic exchange in the exchange vessel is indicated when the slope of the plot of $t_{1/2}$ against $[\mathrm{Hg_{aq}}]$ agrees with the value calculated from equation (4). This occurs only with solutions of mercury in saline or cysteine buffer (Fig. 4). In the presence of octyl alcohol, the slope is about 90% of the theoretical. However, this slope is the same and reproducible both with standard solutions and biological samples.

The construction of the exchange vessel

Complete isotopic equilibration between vapor and aqueous phases was achieved by adjusting two variables: the surface area of contact between the phases was made as large as possible by generating small bubbles, and the aqueous phase was encased in a narrow vertical tube so that the time of rise of the bubbles from the bottom to the top of the sample was long.

The absorption of mercury vapor on hopcalite

This material was chosen because it is efficient absorbent, cheap and commercially available. When hopcalite is present in the absorbent tube to a depth of 1 in., all the radioactivity is collected in the lower 25% of the column. When a second hopcalite tube was placed in series with the first, no radioactivity was ever found in the second tube. An average of 98% of the radioactivity removed from the exchange vessel was recovered in the hopcalite. Small losses can occur if the plastic tubing leading from the exchange vessels is excessively long or if the flow-rate of carrier gas is very low.

Plastic tubing

Plastic tubes made from tygon, polyethylene and nylon have been found to be equally acceptable. The length of tubing was kept as short as possible to avoid potential loss of mercury by diffusion through the plastic or by adsorption on surfaces of the tubes.

Vacuum pump

The purpose of the pump was to maintain a slight (1–5 cm of water) negative pressure throughout the vessels and tubing so that, in the event of a leak, radioactive or stable mercury would not be released into the laboratory. A cheap electrically operated pump was used but a water pump is equally effective.

Radioactive detection and display equipment

The essential items are the well-crystal to house the hopcalite tube and a suitable tube and a suitable counter to record the activity. The rate-meter and the recorder are a convenience in that they allow a graphic recording of the rate of build-up of radioactivity in the hopcalite and can give accurate recording when the exchanger rate is rapid. However, a manual instrument can be used when 1-min counts are made at appropriate intervals, but the half-time of exchange has to be 5 min or more. If the very low concentrations are being measured the half-time can be adjusted by lowering the concentration of mercury vapor and/or the rate of flow of carrier gas.

Uses and limitations

The great advantage of this technique is that it is both rapid and simple. It avoids the tedious procedures involved in the removal of organic material from biological samples by oxidation, with all the attendant uncertainties. This method is ideal for checking urine or tissue samples to see if higher-than-normal concentrations of mercury are present, if there has been exposure to inorganic mercury (vapor or salt), but mercury present in urine or tissue as an organo mercurial compound and having at least one covalent link with a carbon atom will not undergo rapid isotopic exchange, for example the mercurial diuretics.[3]

The method has been tested for samples containing 2·0 μg or more of mercury, and as described here is less sensitive than the techniques described by Jacobs, Goldwater and Gilbert[9] and by Toribara.[10] The theoretical limit to the sensitivity of the method is determined by the specific activity of the ^{203}Hg isotope. With the specific activity commercially available (5 mc/g) and very low concentrations of the vapor passed through the exchange vessel, the lower limit of detection should be approximately 0·025 μg of mercury.

Zusammenfassung—Die Methode erübrigt die Oxidation der organischen Substanz. Tracermengen ^{203}Hg werden der Probe zugesetzt und mit dem stabilen Quecksilber ins Gleichgewicht gebracht. Dampf von ^{200}Hg wird mit Stickstoff in Gegenwart von Cystein bei pH 7,4 durch die Probe geleitet und tauscht mit dem ^{203}Hg aus. Der Dampf wird in einer Röhre mit aktiviertem Hopcalit in einem Gammazähle gesammelt. Der Aktivitätsanstieg wird registriert; die Halbwertszeit des Austausches ist der Quecksilberkonzentration in der Probe direkt proportional. Die Methode eignet sich am besten für Urinproben mit mehr als 10 μg Quecksilber im Liter.

Résumé—La méthode élimine l'oxydation de la matière organique. Des quantités de ^{203}Hg correspondant à sa qualité de traceur sont ajoutées à l'échantillon et équilibrées avec le mercure stable. On fait passer de la vapeur de ^{200}Hg en azote à travers l'échantillon où elle s'échange avec le ^{203}Hg en la présence de cystéine et à pH 7,4. On récueille la vapeur dans un tube de Hopcalite activée placé dans un compteur gamma. On enregistre l'activité croissante et le demi-temps d'échange est directement proportionnel à la concentration du mercure dans l'échantillon. La méthode convient au mieux pour des échantillons d'urine contenant plus de 10 μg Hg/l.

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SHORT COMMUNICATIONS

Adsorption of chloro-complexes of the first row transition elements by Dowex A-1

(*Received* 31 *July* 1967. *Revised* 29 *November* 1967. *Accepted* 20 *December* 1967)

ANION adsorption by Dowex A-1 was first reported by Heitner-Wirguin and Markovits[1] who found that a chloro-complex of copper was strongly adsorbed in the presence of hydrochloric acid. The work reported here is concerned with the adsorption of vanadium(IV), chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) from solutions in different concentrations of hydrochloric acid.

EXPERIMENTAL

The resin used, Chelex 100 (analytical grade Dowex A-1, wet mesh range 20–50 U.S. standard) was supplied by Bio-Rad laboratories in 1965. Samples were conditioned by batch treatment with $1M$ sulphuric acid, washing with demineralized water until acid-free, treatment with $2M$ sodium hydroxide and washing with demineralized water until free from alkali. This cycle was repeated five times and the resin dried to constant weight at 100°.

For adsorption experiments, solutions were prepared by dissolving the metal chloride (vanadium(IV) oxide sulphate was used for vanadium) in hydrochloric acid of the required concentration. After analysis by standard methods,[2] the solutions were diluted with the required concentration of acid to give $0{\cdot}05M$ metal solutions.

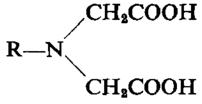
In each experiment 100 ml of metal solution were stirred with 1 g of dried sodium-form resin for 25 min, and the resin was filtered off, washed with hydrochloric acid of the correct concentration and sucked dry. The metal was eluted with $1M$ sulphuric acid and the solution analysed.

RESULTS

In Fig. 1 the adsorption of each metal is plotted against hydrochloric acid concentration. No adsorption was observed for vanadium(IV) or nickel(II).

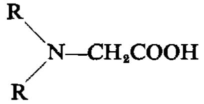
DISCUSSION

Dowex A-1 consists of a styrene–divinylbenzene copolymer matrix in which some of the benzene rings carry substituted nitrogen atoms. Loewenschuss and Schmuckler[3] concluded from elemental analysis of the sodium-form resin that five out of eight benzene rings carried iminodiacetic acid groups. Hering,[4] by comparison of the properties of Dowex A-1 with other chelating resins synthesized by paths giving no side-reactions, concluded that Dowex A-1 contained iminodiacetic acid groups (I), aminoacetic acid groups (II) and amine groups (III).



(I)

$R—NH—CH_2COOH$



(II)

$R—NH_2$

(III)

He attributed failure to elute copper with $2M$ hydrochloric acid from samples of Dowex A-1 marketed before 1964 to the presence of amine groups (III) and showed that this did not happen with resins containing only groups I or II. He suggested that in the presence of concentrated acid, groups II and III would react to give amides, which are known to form complexes with copper in concentrated hydrochloric acid. Hering attributed the easier elution of copper with hydrochloric acid from Dowex A-1 marketed during and after 1964 to the higher proportion of I as compared with II and III.

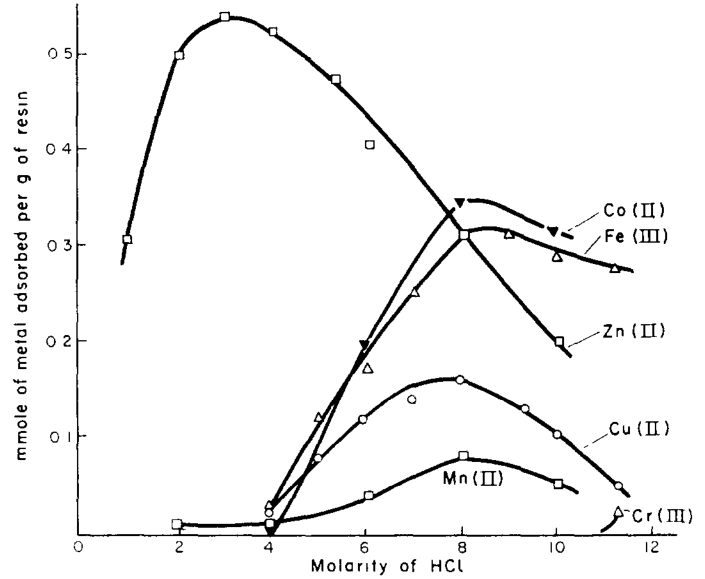
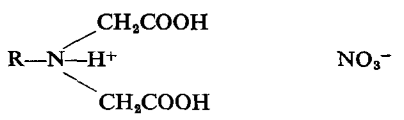


FIG. 1.—Effect of hydrochloric acid concentration on adsorption of metal chloro-complexes.

The graphs relating the amount of metal adsorbed per gram of dry Dowex A-1 resin to the molarity of hydrochloric acid present are very similar to those reported by Kraus[6] and his co-workers for adsorption on the anion-exchanger Dowex-1 from solutions of similar acid concentrations. Comparison of the maximum adsorption of a metal chloro-complex from acid solution by Dowex A-1 with that for the adsorption of the same metal as a cation, gave the following results: zinc(II) 25%, cobalt(II) 17%, copper(II) 6%, manganese(II) 4%.

If adsorption of anions by Dowex A-1 is due solely to R—NH$_2$ groups they must be present in proportion up to 25% of the sum of iminodiacetic and amino acid groups. Other adsorption mechanisms are possible. Kraus, Michelson and Nelson[6] showed that the cation-exchange resin Dowex-50 strongly adsorbed the chloro-complex of iron(III) but that those of manganese(II), copper(II) and iron(II) were only slightly adsorbed. The effect, which was more marked in salt than in acid solutions, was attributed to the interaction of the anions with the resin network. Schwarz (quoted by Schmuckler[7]) reported that at pH values below 2·21, Dowex A-1 in nitrate media showed infrared vibrations characteristic of nitrate and concluded that the resin existed as



under these conditions.

Protonation of the nitrogen atom would be enhanced in the presence of concentrated acid and the resin would behave as an anion-exchanger. It is possible that all three mechanisms play some part in adsorption but that amine groups and *N*-protonated iminodiacetic acid groups are chiefly responsible.

Marcus[8] recently reviewed the nature of metal chloro-complexes shown by solvent extraction and ion-exchange studies to be present at various concentrations of hydrochloric acid. For the relevant metals, these complexes are $MnCl_3^-$, $FeCl_4^-$, $CoCl_3^-$, $CuCl_3^-$ and $ZnCl_4^{2-}$.

The higher adsorption of the zinc chloro-complex can be attributed to its greater charge.

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Summary—A study has been made of the adsorption of chloro-complexes of the first row transition metals by the chelating resin Dowex A-1, and possible mechanisms for adsorption have been reviewed. Relative adsorption follows the series Zn(II) > Co(II) = Fe(III) ≫ Cu(II) > Mn(II). Negligible adsorption occurred with Cr(III) and none with V(IV) and Ni(II). Maximum adsorption of Zn(II) occurred from 3*M* hydrochloric acid and for the other metals from 8*M* acid.

Zusammenfassung—Die Adsorption von Chlorokomplexen der Metalle der ersten Übergangsreihe an dem chelatbildenden Harz Dowex A-1 wurde untersucht und eine Übersicht über die möglichen Adsorptionsmechanismen gegeben. Die relative Adsorption folgt der Reihe Zn(II) > Co(II) = Fe(III) ≫ Cu(II) > Mn(II). Cr(III) wird in vernachlässigbarem Ausmaß adsorbiert, V(IV) und Ni(II) gar nicht. Zn(II) wurde aus 3*M* Salzsäure maximal adsorbiert, die anderen Metalle aus 8*M* Salzsäure.

Résumé—On a effectué une étude sur l'adsorption de chloro-complexes des métaux de transition de la première rangée par la résine chélatante Dowex A-1, et l'on a passé en revue les mécanismes d'absorption possibles. L'adsorption relative suit la série Zn(II) > Co(II) = Fe(III) ≫ Cu(II) > Mn(II). Une adsorption négligeable se produit avec Cr(III) et elle est nulle avec V(IV) et Ni(II). L'adsorption maximale du Zn(II) est obtenue à partir d'acide chlorhydrique 3*M* et, pour les autres métaux, à partir d'acide 8*M*.

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Micro and semi-micro determination of organic nitrogen by use of potassium bromate

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It has already been shown[1,2] that the distillation step in the Kjeldahl method can be eliminated by titrimetric and colorimetric methods, but most of the titrimetric methods suffer from draw-backs. The formaldehyde method[3-8] is not satisfactory because of reversibility and the involved procedure. Hypobromite[9-14] is not stable at room temperature and must be kept at temperatures below 5° to avoid loss of bromine; in any case, the results are erratic.[15-16] Calcium hypochlorite[17] and more recently, sodium hypochlorite, have been used by various workers.[18-23] The reagents are more stable than hypobromite and behave just like it in the presence of potassium bromide. However, although the hypochlorite method is rapid, accurate and suitable for multiple nitrogen determinations, and 0·2*N* hypochlorite in sodium hydroxide remains unchanged for a week when kept in a dark bottle at room temperature, it is still customary to standardize the reagent daily before use.

The drawbacks of these methods can be circumvented by the application of a method due to Köszegi and Salgo,[24] in which hypobromite is produced *in situ* from a standard solution of bromate in the Schulek bromination flask.[25] The method has already been applied to the determination of

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The drawbacks of these methods can be circumvented by the application of a method due to Köszegi and Salgo,[24] in which hypobromite is produced *in situ* from a standard solution of bromate in the Schulek bromination flask.[25] The method has already been applied to the determination of non-protein nitrogen in serum.[26] We describe here a convenient flask for determination of nitrogen in organic compounds.

EXPERIMENTAL

Apparatus

A 250-ml round-bottom flask, with a B19 neck fitted with a 15-cm tube attached to a B19 cone, is used both for the micro and the semi-micro procedures. The flask, when fitted with the cone, is used for digestion. Afterwards the cone is replaced with an *N*-shaped tube (Fig. 1) and the same flask is used for titration.

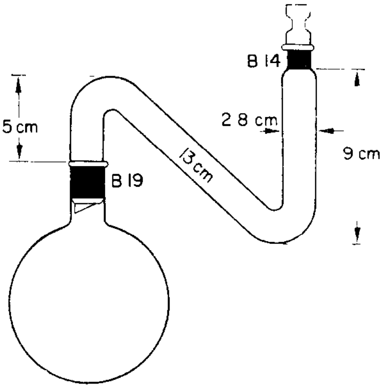

FIG. 1

Procedures

Micro-determination of nitrogen. Weigh 5–10 mg of the sample accurately into the flask. Add 0·7 g of the catalyst (a mixture of 0·625 g of potassium sulphate and 0·075 g of mercury(II) sulphate) and 3 ml of concentrated sulphuric acid. Attach the cone to the flask and digest its contents for 1–2 hr. For nitro, nitroso and azo compounds, add 0·2–0·3 g of glucose and 4 ml of sulphuric acid before the digestion. Cool and dilute the digest by rinsing the cone with 25 ml of distilled water. Place the flask in cold water, and run in 20 ml of 0·04*N* potassium bromate. Place 25 ml of 25% sodium hydroxide solution in the *N*-tube and stopper its upper end. Add 0·5 g of potassium bromide and immediately fit the stoppered *N*-tube. By slightly tilting the flask allow the sodium hydroxide solution to flow gradually into the cold acidic solution below. Shake the contents of the flask and allow it to stand for 20 min. Add 6 ml of 7*M* hydrochloric acid directly to the flask and immediately attach the *N*-tube containing 10 ml of freshly prepared 10% potassium iodide solution. Run in the iodide solution 5 min after addition of the hydrochloric acid. After another 5 min titrate the liberated iodine with 0·02*N* sodium thiosulphate, using starch as indicator. Do a blank determination under identical conditions.

Semi-micro determination of nitrogen. Weigh 30–50 mg of the sample and digest with 2·8 g of the catalyst and 6 ml of concentrated sulphuric acid. Use 1 g of glucose and 10 ml of sulphuric acid for compounds requiring reduction. Add 20 ml of 0·1*N* potassium bromate and 1 g of potassium bromide for the liberation of bromine, and 25 ml of 50% sodium hydroxide solution for neutralizing the acid and for converting bromine into hypobromite. The rest of the reagents are: 20% potassium iodide solution, 10 ml; 7*M* hydrochloric acid, 12 ml; 0·05*N* sodium thiosulphate.

$$1\ \text{ml}\ 0{\cdot}1N\ \text{KBrO}_3 = 0{\cdot}4667\ \text{mg}\ \text{N}_2$$

DISCUSSION

This method is superior because there is no need to prepare fresh solutions of hypohalites or to standardize the solutions daily before use. The method is quite elegant; potassium bromate is a primary standard, its neutral solution is indefinitely stable, and no special indicators are required. The acidic digest does not require to be carefully neutralized as in the previous methods. Potassium bromate and bromide are directly added to the cold acidic digest and the liberated bromine is converted into hypobromite *in situ* by the addition of an excess of sodium hydroxide. Arsenite cannot be used as the titrant, because of the inapplicability of indicators such as Bordeaux and tartrazine. Sodium thiosulphate solution, which is stable either at pH 9–10 or with a few drops of chloroform added, is used instead. The special *N*-tube prevents loss of bromine, and converts the digestion-*cum*-titration flask into a bromination flask. The apparatus is easier to fabricate and handle than various special bromination flasks.[27]

The results for micro and semi-micro determinations (Table I) are correct within the experimental error. Nevertheless, the accuracy is governed by the completeness of the digestion of organic compounds. Results were invariably higher if digestion was incomplete, showing that some bromine was consumed in the destruction of oxidizable matter still left in the digest.

TABLE I.—RECOVERY OF NITROGEN

Compounds	Required, %	Found	
		Micro method, %	Semi-micro method, %
Ammonium sulphate	21·21	21·0, 21·3	21·1, 21·1
Phenacetin	7·82	7·8, 7·9	8·0, 7·9
Hippuric acid	7·82	7·8, 7·8	7·7, 7·9
8-Hydroxyquinoline	9·65	9·5, 9·7	9·8, 9·6
Acetanilide	10·36	10·5, 10·3	10·6, 10·3
Quinine sulphate	7·16	7·1, 7·2	7·0, 7·1
Atropine	4·84	4·86, 4·7	5·0, 4·7
Diphenylamine	8·28	8·1, 8·2	8·2, 8·1
DL-Alanine	15·72	15·6, 15·8	15·9, 15·6
α-Nitroso β-naphthol	8·09	8·1, 8·2	8·2, 8·2
p-Nitroaniline	20·29	20·4, 20·3	20·3, 20·2
o-Nitrobenzoic acid	8·38	8·2, 8·4	8·2, 8·3
Azobenzene	15·38	15·6, 15·3	15·5, 15·3

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Summary—After Kjeldahl digestion of an organic compound, nitrogen is determined by oxidation of the resultant ammonium sulphate with hypobromite produced *in situ* by the addition of an excess of potassium bromate and bromide in a special flask. The unreacted potassium bromate is determined iodometrically.

Zusammenfassung—Nach dem Kjeldahlaufschluß einer organischen Verbindung wird Stickstoff durch Oxidation des entstandenen Ammoniumsulfats mit Hypobromit bestimmt. Dieses wird in situ durch Zugabe von überschüssigem Kaliumbromat und Bromid in einem Spezialkolben erzeugt. Das nicht verbrauchte Kaliumbromat wird jodometrisch bestimmt.

Résumé—Après digestion Kjeldahl d'un composé organique, on dose l'azote par oxydation du sulfate d'ammonium résultant avec de l'hypobromite produit *in situ* par l'addition d'un excès de bromate et de bromure de potassium dans une fiole spéciale. Le bromate de potassium qui n'a pas réagi est déterminé par iodométrie.

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The 1:3 uranium(VI)–8-hydroxyquinoline compound: its composition and thermal conversion into bis(8-hydroxyquinolinato)dioxouranium(VI)

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UNDER appropriate conditions, reaction between uranium(VI) and 8-hydroxyquinoline in aqueous solution yields a red compound with the assigned formula $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$.[1-5] The compound has been reported in the literature many times[6-18] and the 3:1 oxine:uranium composition has become accepted.

In the course of studies on the structure of the red compound,[19] we noted that our analytical data consistently indicated a composition that was just lower than 3:1. Since the method of preparation was one[5] that has been very widely used by other workers, we investigated this observation more closely. The present report provides evidence that the red compound prepared according to reference 5 is indeed slightly non-stoichiometric.

The preparation of bis(8-hydroxyquinolinato)dioxouranium(VI), $UO_2(C_9H_6NO)_2$, by the thermal conversion of the red compound has been often reported.[2-9,11-13,16,17] Surprisingly, however, the degree of experimental control required for the preparation of the *pure* bis complex has received little attention, and analytical data supporting the reported composition of the product are scanty. Many investigators have used a procedure[5] which recommends a heating period of 48 hr at 210–215°. In our work, we found that this procedure leads to partial decomposition of the bis complex. In the present report, we describe conditions that successfully yield the *pure* bis complex.

EXPERIMENTAL

Uranyl nitrate hexahydrate (Analar grade, B.D.H.) was used without further purification. 8-Hydroxyquinoline (Certified Grade, Fisher Scientific Co.) was purified by sublimation before use. All other chemicals were of sufficient purity for the purpose intended. The red compound was prepared by the method of Moeller and Wilkins.[5] After filtration and washing with a small volume of ethyl alcohol and several small portions of distilled water, the compound was dried in a stream of air for 1 hr, and then kept for 24 hr in a desiccator containing anhydrous magnesium perchlorate. The 8-hydroxyquinoline (HQ) and the uranium contents were estimated by bromometric titration[20] and ignition to U_3O_8,[18] respectively. From the data, the HQ:U molar ratio in the red compound was determined (Table I).

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The 1:3 uranium(VI)–8-hydroxyquinoline compound: its composition and thermal conversion into bis(8-hydroxyquinolinato)dioxouranium(VI)

(*Received* 29 *November* 1967. *Accepted* 15 *January* 1968)

UNDER appropriate conditions, reaction between uranium(VI) and 8-hydroxyquinoline in aqueous solution yields a red compound with the assigned formula $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$.[1-5] The compound has been reported in the literature many times[6-18] and the 3:1 oxine:uranium composition has become accepted.

In the course of studies on the structure of the red compound.[19] we noted that our analytical data consistently indicated a composition that was just lower than 3:1. Since the method of preparation was one[5] that has been very widely used by other workers, we investigated this observation more closely. The present report provides evidence that the red compound prepared according to reference 5 is indeed slightly non-stoichiometric.

The preparation of bis(8-hydroxyquinolinato)dioxouranium(VI), $UO_2(C_9H_6NO)_2$, by the thermal conversion of the red compound has been often reported.[2-9,11-13,16,17] Surprisingly, however, the degree of experimental control required for the preparation of the *pure* bis complex has received little attention, and analytical data supporting the reported composition of the product are scanty. Many investigators have used a procedure[5] which recommends a heating period of 48 hr at 210–215°. In our work, we found that this procedure leads to partial decomposition of the bis complex. In the present report, we describe conditions that successfully yield the *pure* bis complex.

EXPERIMENTAL

Uranyl nitrate hexahydrate (Analar grade, B.D.H.) was used without further purification. 8-Hydroxyquinoline (Certified Grade, Fisher Scientific Co.) was purified by sublimation before use. All other chemicals were of sufficient purity for the purpose intended. The red compound was prepared by the method of Moeller and Wilkins.[5] After filtration and washing with a small volume of ethyl alcohol and several small portions of distilled water, the compound was dried in a stream of air for 1 hr, and then kept for 24 hr in a desiccator containing anhydrous magnesium perchlorate. The 8-hydroxyquinoline (HQ) and the uranium contents were estimated by bromometric titration[20] and ignition to U_3O_8,[18] respectively. From the data, the HQ:U molar ratio in the red compound was determined (Table I).

TABLE I.—ANALYSIS OF THE RED COMPOUND

Condition	U, %	HQ,* % (as Q^-)	Molar ratio HQ:U
Dried without heating	33·94† ±0·03	60·88† ±0·04	2·963 ±0·003
50% excess of HQ; dried without heating	33·88‡ ±0·03	60·88‡ ±0·08	2·968 ±0·006

* HQ = 8-hydroxyquinoline.

† Average of 11 results, error is the standard error ($\sigma/\sqrt{n}$).[21]

¶ Two results.

‡ Three results.

For $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$, U = 33·84% and HQ, expressed as Q^- = 61·47%.

Samples of the red compound were also taken for the determination of the ratio of sublimed 8-hydroxyquinoline to the residual bis compound obtained on thermal conversion. The conversion was effected quantitatively by heating (oil-bath) 500–700 mg of the red compound at 210–215° for 4 hr *in vacuo* (0·1 mm Hg). The sublimed 8-hydroxyquinoline was collected as a compact deposit in the initial portion of a U-tube immersed in a dry-ice bath. In all cases, a very small droplet of moisture was noted below the deposit of 8-hydroxyquinoline in the U-tube. The deposit and the residual bis compound were separately dissolved in 4*M* hydrochloric acid and determined bromometrically, and the ratio HQ:UO_2Q_2 was calculated (Table II). In a similar experiment, only the proportion of sublimed HQ was determined.

TABLE II.—MOLAR RATIO HQ:UO_2Q_2 IN THE RED COMPOUND

HQ sublimed, *mg*	UO_2Q_2 residue, *mg*	Molar ratio HQ:UO_2Q_2
61·1	245·5	0·957
30·6	121·2	0·969

The same thermal procedure was used to prepare the pure bis compound. The 8-hydroxyquinoline and uranium contents were determined as described above.

DISCUSSION

The data in Table I indicate that the red compound is slightly deficient in 8-hydroxyquinoline, at least when prepared by the method[5] used in this work. The samples were dried without heating, to ensure that not a trace of the thermally volatile neutral ligand was lost owing to drying at an elevated temperature. The possibility that the deficiency is caused by hydrolysis of a small amount of the uranyl ion during precipitation was investigated by increasing the excess of reagent from 13 to 50%. The results were unaffected; further experiments with excesses that approach the solubility limit of 8-hydroxyquinoline should be made. Because of the mild drying conditions used, it is likely that the samples retained traces of moisture. Although the presence of moisture would lower the proportions of both U and Q^- in the red compound, it would not affect the molar ratio of the species.

The data in Table II, obtained by determining the relative amounts of sublimed 8-hydroxyquinoline and the bis compound, are in excellent agreement with those in Table I. That the red compound did retain traces of moisture was confirmed by the presence of the very small droplet condensed in the U-tube below the 8-hydroxyquinoline deposit. If it is assumed that the deficient 8-hydroxyquinoline is replaced by coordinated water, the formula of the red compound can be written as $UO_2(C_9H_6NO)_2 \cdot 0{\cdot}96C_9H_7NO \cdot 0{\cdot}04H_2O$. From the weights taken of the red compound (307·9 and 152·2 mg), calculation shows, however, that the bulk of the observed droplet must have been present in the red compound as unbound moisture (0·3–0·4 mg of moisture per 100 mg).

The validity of the conclusions depends heavily on the accuracy of the analytical determinations, since the effect being sought is small. In tests with known amounts of purified 8-hydroxyquinoline, the absolute error of the bromometric method did not exceed ±0·1 mg. For the data in Table I, it can be shown that when the weights (100–135 mg) of the red compound are corrected for the presence of moisture (~0·4 mg), the deficiency of 8-hydroxyquinoline being sought is 0·7–0·9 mg. The bromometric error represents 11–15% of this range. A corresponding test for the accuracy of the uranium determination could not be devised, but the experimental value (33·94%) agrees excellently with the value expected (33·95%) for the non-stoichiometric compound containing 0·4% moisture. The statistical *t*-test indicates that the difference between the experimental value and the value for a 3:1 composition (33·84%), although small, is significant.

For the two samples in Table II, the deficiencies in 8-hydroxyquinoline were 2·1 and 1·0 mg. Similarly, in experiments in which only the proportion of sublimed HQ in the red compound was determined, the deficiency was about 3·5–5 mg (for sample weights of about 500–700 mg). In these experiments, the average of 4 results was 19·92 ± 0·05% (standard error). Based on a true 1:3 compound containing 0·4% moisture, the theoretical proportion of sublimed HQ is 20·55%; for a compound with the composition $UO_2(C_9H_6NO)_2 \cdot 0{\cdot}96C_9H_7NO \cdot 0{\cdot}04H_2O$ and containing 0·4% moisture, the sublimed HQ is 19·87%, considerably closer to the experimental result.

Since the three methods of analysis give essentially the same result, we conclude that the red complex, prepared as described, is slightly deficient in 8-hydroxyquinoline. Claassen and Visser[4] also claim to have prepared the red compound with a small deficiency in 8-hydroxyquinoline.

The deficiency can be readily explained by competition from coordinating ligands such as water or ammonia for the coordination site occupied by the neutral 8-hydroxyquinoline ligand. This ligand is bonded to the uranium atom through only the oxygen donor.[22] The proton is on the nitrogen atom and is hydrogen-bonded to the oxygen of the neighbouring bidentate ligand.[19] Competition by water and ammonia has been previously demonstrated in the case of U(VI) complexes of 7-substituted derivatives of 8-hydroxyquinoline.[19] In these complexes, steric interference from the 7-substituent prevents the stable attachment of the neutral ligand, and complexes with the composition $UO_2(R{-}C_9H_5NO)_2{\cdot}H_2O$ and $UO_2(R{-}C_9H_5NO)_2{\cdot}NH_3$ (R = methyl, t-butyl) are obtained.

The data presented in this study suggest that one in about 25–30 uranium atoms is deficient in 8-hydroxyquinoline. This effect is too small to allow detection of the competing ligand by infrared or X-ray methods.

It should be possible to prepare an exactly 1:3 compound by using pH values either below or above the range (4·9–5·2) used in this study. If the ligand in its fully protonated form (H_2Q^+) reacts with the uranium and the phenolic proton is released during the formation of the U—O bond, preparation of a stoichiometric compound would be favoured by a lower pH since the concentration of H_2Q^+ would be higher. On the other hand, if the neutral species HQ is involved and the phenolic proton is transferred to the nitrogen atom during the formation of the U—O bond, the stoichiometric compound would be favoured by a higher pH. Judging from the observation by Bordner *et al.*[10] that at pH 6·8 an orange-red compound with the composition $[UO_2(C_9H_6NO)_2]{\cdot}C_9H_7NO$ is precipitated, while at pH 5·0 the red 1:3 compound is obtained, it appears that a lower rather than a higher pH value would favour the formation of the true 1:3 compound.

Initial attempts to prepare the pure bis compound $UO_2(C_9H_6NO)_2$ thermally, were based on a procedure[5] involving heating the red compound in air at 210–215° for 48 hr. Analysis of the product gave the following results: U, 44·63 ± 0·06% (2 results; theoretical, 42·64%); HQ as Q^-, 46·86 ± 0·06% (3 results; theoretical, 51·63%). These results show that appreciable decomposition of the bis compound has occurred. The use of shorter heating times resulted in compositions closer to the theoretical but the pure bis compound could not be obtained.

The pure bis compound can be easily prepared by heating the red compound (500–700 mg) *in vacuo* at 210–215° for 4 hr (for 10 results, U, 42·52 ± 0·04%; Q^-, 51·50 ± 0·04%; molar ratio Q^-: U, 2·001 ± 0·002). A red colour was still discernible after 2 hr. For smaller samples, complete conversion would likely require less than 4 hr. Heating periods up to 37 hr have little effect on the composition of the bis compound. The advantage in preparing the bis compound *in vacuo* rather than in an oxidizing atmosphere is readily apparent.

These results do not contradict those of earlier TGA and DTA studies[7,8,11,12] in which it was shown, for example, that now eight loss occurs up to 220°. The experimental conditions of the TGA and DTA studies are different to those used in the present study, so that an exact correspondence in the temperature of a thermal reaction is not to be expected.

In view of the knowledge now available regarding the structure of the red compound,[19,22] it is worth commenting on the endothermic DTA peak at 150° observed by Horton and Wendlandt.[12] These workers speculated that this peak was due to a rearrangement reaction rather than to a reaction involving the elimination of a gas, since a gaseous product could not be detected. We feel that this interpretation is basically correct and suggest that the endothermic peak corresponds to rupture of the hydrogen bond stabilizing the neutral ligand,[19] and to any subsequent rearrangement of this ligand or of the complex as a whole.

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Summary—Evidence is provided to show that in the red compound formed between uranium(VI) and 8-hydroxyquinoline, the ligand-to-uranium ratio is slightly lower than 3:1, at least when the compound is prepared by a widely accepted procedure. Competition between 8-hydroxyquinoline and other ligands such as water or ammonia is probably responsible for the non-stoichiometry. Further, it is shown that a procedure frequently used for the thermal conversion of the red compound into bis(8-hydroxyquinolinato)dioxouranium(VI) yields a compound in which the ligand-to-uranium ratio is less than 2:1. Conditions which lead to the thermal preparation of the stoichiometric bis compound are described.

Zusammenfassung—Es werden Beweise dafür vorgebracht, daß in der roten Verbindung aus Uran(VI) und 8-Hydroxychinolin das Verhältnis Ligand:Uran etwas kleiner als 3:1 ist, mindestens wenn die Verbindung nach einer weithin angewandten Vorschrift dargestellt wird. Fur die Abweichung von der Stöchiometrie ist vermutlich die Konkurrenz zwischen 8-Hydroxychinolin und anderen Liganden wie Wasser oder Ammoniak verantwortlich. Es wird ferner gezeigt, daß eine oft zur thermischen Umwandlung der roten Verbindung zu Bis(8-hydroxychinolato)dioxouran (VI) verwendete Vorschrift ein Produkt liefert, in dem das Verhältnis Ligand:Uran etwas kleiner als 2:1 ist. Es werden Bedingungen angegeben, die die stöchiometrische Bis-Verbindung thermisch herzustellen gestatten.

Résumé—On apporte des arguments pour montrer que, dans le composét rouge formé entre l'uranium(VI) et la 8-hydroxyquinoléine, le rapport ligand-uranium est légèrement plus faible que 3:1, au moins lorsque le composé est préparé par une technique généralement admise. Une compétition entre la 8-hydroxyquinoléine et d'autres ligands tels que l'eau ou l'ammoniaque est probablement responsable de la non-stoechiométrie. De plus, on montre qu'une technique fréquemment utilisée pour la conversion thermique du composé rouge en bis(8-hydroxyquinoléinato)dioxouranium(VI) fournit un composé dans lequel le rapport ligand-uranium est inférieur à 2:1. On décrit les conditions menant à la préparation du bis-composé stoechiométrique.

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Application of electroluminescence techniques to the determination of aromatic hydrocarbons

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THE electrically stimulated emission of radiation in solution, known as electroluminescence, has been widely observed,[1,2] but only very recently has any serious attempt been made to elucidate the mechanism of the process.[3,4] Electroluminescence may be observed for hydrocarbons when a small-amplitude alternating voltage is applied between two inert electrodes immersed in a solution of the compound in a non-aqueous solvent. Emission is obtained which is characteristic of the solute, and can frequently be modified in colour and intensity by alteration of the solvent, the supporting electrolyte, and the wave-form of the signal applied.

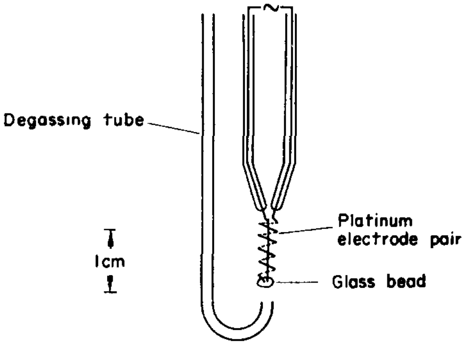
Up to the present no evaluation of the analytical potential of this technique has been reported, although the application of electroluminescence to organic trace analysis shows considerable promise. This paper presents the results of an investigation of the electroluminescence of some aromatic hydrocarbons, and its use for their detection and determination.

EXPERIMENTAL

Apparatus

Electroluminescence and fluorescence measurements were made with a double monochromator spectrofluorimeter (American Instrument Co.). A fused quartz cell (10 × 10 mm) was used with the electrode assembly shown in Fig. 1*a*. This assembly is sealed through a Teflon block which forms

(a) Spiral type:



(b) Grid type

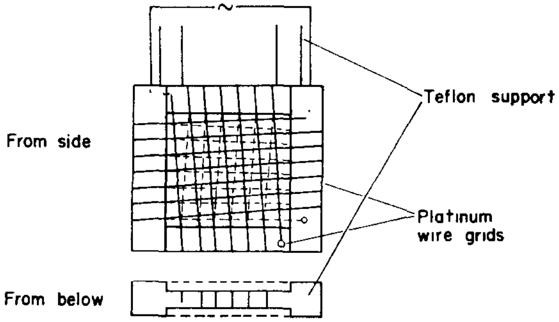


FIG. 1.—Electrode assemblies employed.

the lid of the cell. The electrodes consist of a 10 mm length of platinum wire (0·004 in. diameter), insulated from the helix (4 mm diameter) of platinum wire which surrounds it. A nitrogen delivery tube for deoxygenation is mounted immediately below the electrode assembly. The electrodes are placed in the cell so that the assembly is at the focus of the emission monochromator and photomultiplier optical arrangement. An a.c. voltage of 3 V (50 cps) was supplied to the electrodes from the laboratory mains supply *via* a step-down transformer.

Reagents

Solvent. Dimethylformamide (DMF), laboratory reagent grade, was used throughout without further purification.

Electrolytes. Lithium chloride, tetramethylammonium chloride and tetrabutylammonium bromide, laboratory reagent grade, were used without further purification, with the exception that the lithium chloride was oven-dried at 100° before use. Tetra-n-butylammonium perchlorate was prepared by acidification of tetra-n-butylammonium hydroxide with 70% perchloric acid, and recrystallized from a water-methanol mixture.

Nitrogen. White-spot nitrogen (British Oxygen Co., Ltd.). Residual oxygen was removed by scrubbing the gas with an alkaline solution of anthraquinone-2-sulphonic acid (2% in $2M$ sodium hydroxide). The nitrogen was then dried by bubbling through concentrated sulphuric acid and over magnesium perchlorate, and finally saturated with the solvent by bubbling through dimethylformamide.

Hydrocarbons. Anthracene, pyrene, 9-phenylanthracene and coronene were prepared as $10^{-3}M$ solutions in dimethylformamide. The rubrene was used as a $5 \times 10^{-4} M$ solution in dimethylformamide.

General procedure

The hydrocarbon solution (2·5 ml) containing electrolyte was placed in the quartz cell and deoxygenated with a fast stream of nitrogen for three minutes. The voltage was then applied to the electrodes, and the electroluminescence spectrum recorded over the required wavelength range, with wide slits (20 mμ band-width) in the emission monochromator. The fluorescence emission spectrum was then recorded for the same solution at the same resolution. These spectra were recorded at the wavelength of maximum excitation established experimentally.

RESULTS AND DISCUSSION

Figure 2 shows the results obtained for the hydrocarbons examined. The electroluminescence spectra are superimposed on the fluorescence emission spectra obtained under the same conditions. The spectra are uncorrected for the characteristics of lamp emission and photomultiplier response. The relevant correction curves appear elsewhere.[5] The shape and intensity of the spectra confirm the general observations of Chandross *et al.*[6] who suggested that two related pathways are possible for the interaction between the anodic oxidation product R^+ and the cathodic reduction product R^- of the hydrocarbons. If the reaction $R^+ + R^- \rightarrow R + R^*$ occurs to produce a singlet or triplet excited hydrocarbon monomer molecule, the electroluminescence spectrum obtained resembles that of the normal fluorescence of the hydrocarbon. This type of reaction may be postulated from the results shown in Fig. 2 for rubrene. Rubrene is non-planar and possesses large bulky substituents, and thus the possibility of excimer[7] formation is unlikely. The reaction $R^+ + R^- \rightarrow (R_2)^*$, which results in excimer formation has also been suggested to explain the electroluminescence of hydrocarbons.[6] The excimer emission is characterized by a broad structureless band shifted towards the red from the normal fluorescence emission maximum. Chandross suggests that excimer formation *via* this reaction path is favoured by molecules which are planar and do not possess bulky substituent groups. The results for anthracene suggest that excimer formation occurs for this hydrocarbon. Where excimer formation is possible, the shape and intensity of the electroluminescence spectrum is affected by several factors. The dependence of the shape of the spectrum on the nature of the electrolyte used is illustrated for anthracene in Fig. 2 (spectra 5 and 6). The extent of stirring of the solution can also influence the spectra obtained. For coronene, for example, Fig. 2 (spectrum 4) shows that with adequate stirring the electroluminescence emission resembles the emission from the monomer state, whereas with an inadequately stirred solution the emission is shifted towards the red where excimer emission would be expected.

From the point of view of organic trace analysis, it is apparent from the results obtained that the selectivity of the electroluminescence technique applied to the analysis of hydrocarbons must ultimately be superior to that of conventional spectrofluorimetry, owing to the facility with which the resolution can be increased by alteration of the solution and electrical parameters. The sensitivity of the technique depends principally on the instrumental arrangement employed. With the present

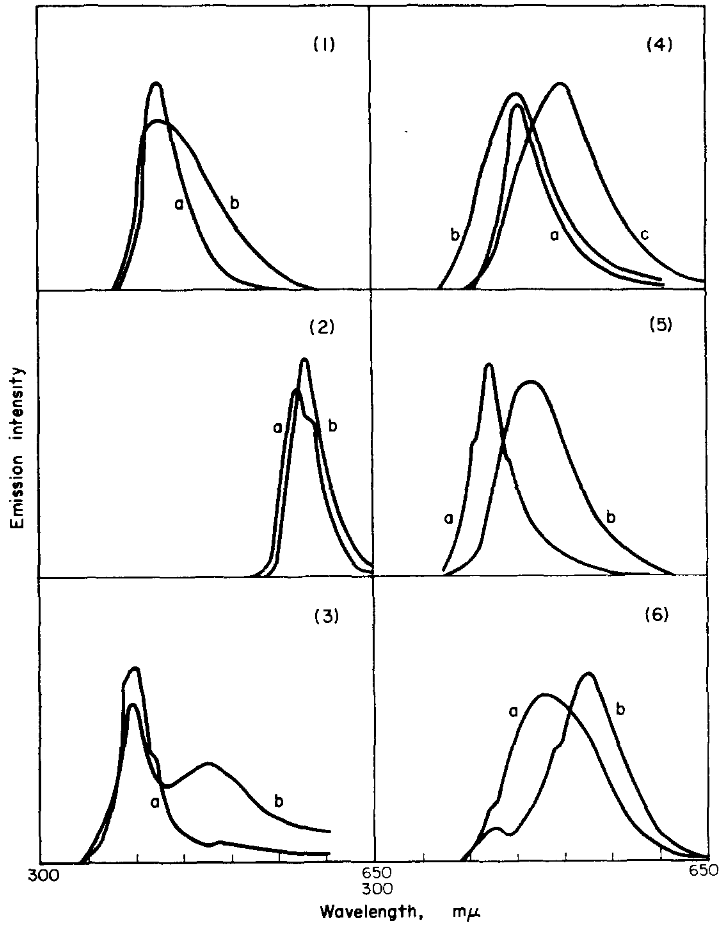


FIG. 2.—Electroluminescence and fluorescence spectra obtained.

(1) 9-Phenylanthracene, $10^{-3}M$ in DMF. *a*—Fluorescence emission spectrum (excitation at 320 mμ); *b*—electroluminescence (E.L.) emission spectrum, tetrabutylammonium perchlorate electrolyte ($10^{-3}M$), 3 V a.c., continuous stirring.

(2) Rubrene, $5 \times 10^{-4}M$ in DMF. *a*—E.L. emission spectrum, tetrabutylammonium perchlorate ($10^{-3}M$), 3 V a.c., continuous stirring; *b*—fluorescence emission spectrum (excitation at 430 mμ).

(3) Pyrene, $10^{-3}M$ in DMF. *a*—Fluorescence emission spectrum (excitation at 355 mμ); *b*—E.L. emission spectrum, tetrabutylammonium bromide electrolyte, 6 V a.c., continuous stirring.

(4) Coronene, $10^{-3}M$ in DMF. *a*—Fluorescence emission spectrum (excitation at 365 mμ); *b*—E.L. emission spectrum, tetrabutylammonium perchlorate electrolyte, 3 V a.c., continuous stirring; *c*—as *b* but without stirring.

(5) Anthracene, $10^{-3}M$ in DMF. *a*—Fluorescence emission spectrum (excitation at 365 mμ); *b*—E.L. emission spectrum, tetrabutylammonium perchlorate, 3 V a.c., continuous stirring.

(6) Anthracene, $10^{-3}M$ in DMF. *a*—E.L. emission spectrum in tetramethylammonium chloride electrolyte, 3 V a.c., continuous stirring; *b*—E.L. emission spectrum, lithium chloride electrolyte ($10^{-2}M$), 3 V a.c., continuous stirring.

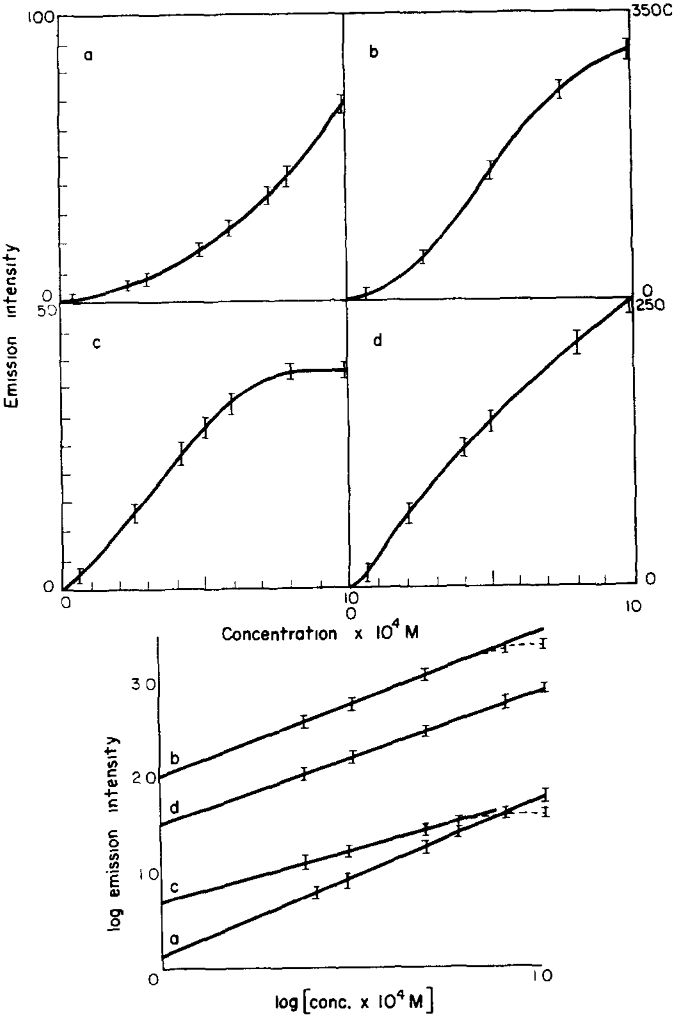


FIG. 3.—Electroluminescence calibration curves for (*a*) anthracene, (*b*) 9-phenylanthracene, (*c*) pyrene, (*d*) coronene in DMF (3 V a.c. applied voltage).

apparatus and electrode assembly the sensitivities obtainable are unfavourable compared with those which can be obtained for the spectrofluorimetric determination of the same hydrocarbons with the same equipment. The sensitivity of the apparatus for fluorescence measurements relies on the intense excitation source (xenon arc) employed, and the monochromator and photomultiplier optical arrangement are relatively inefficient when the same apparatus is used for electroluminescence studies. Calibration curves at the wavelength of maximum electroluminescence were obtained with the electrode assembly shown in Fig. 1*a*. The calibration curves initially obtained appeared to be linear, but the precision of the measurements was low owing to stray light and high noise levels. Under carefully controlled conditions the precision of the intensity measurements was improved, and the calibration data shown in Fig. 3 were obtained. These curves are non-linear, but are reproducible and therefore of analytical utility. A log-log plot of the data gave a linear relationship for each of the compounds studied. Reliable quantitative measurements were not possible for rubrene under the conditions employed, owing to rapid discoloration of the solution. The quantitative aspects of the processes which occur at the electrodes to give rise to the observed relationship between electroluminescence intensity and the concentration are at present being studied. Our preliminary results for experiments similar to those reported here, but made with a different electrode assembly (Fig. 1*b*) viewed by a similar photomultiplier through a narrow band-pass interference monochromator, reveal that similar spectra can be recorded and calibration data obtained for 10^{-7}–$10^{-5}M$ solutions.

One of the factors which at present limits the application of electroluminescence to organic analysis is the small range of compounds which have been found to exhibit the effect. We have shown, however, that the method can be extended to the detection of aromatic amines and phenols which normally do not show significant electroluminescence, *e.g.*, 2-naphthylamine and 1-naphthol, by methylation of the deactivating group. These studies will be reported in a later communication.

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Summary—An account is given of the quantitative determination of certain fused-ring aromatic hydrocarbons by means of the electroluminescence induced by application of a small a.c. voltage to inert electrodes placed in a solution of the hydrocarbon in dimethylformamide.

Zusammenfassung—Es wird eine Übersicht gegeben über die quantitätive Bestimmung einiger aromatischer Kohlenwasserstoffe mit kondensierten Ringen mit Hilfe der Elektrolumineszenz, die durch Anlegen einer kleinen Wechselspannung an inerte Elektroden in einer Lösung des Kohlenwasserstoffs in Dimethylformamid erzeugt wird.

Résumé—On présente un compte-rendu sur la détermination quantitative de certains hydrocarbures aromatiques à noyaux condensés, au moyen de l'électroluminescence induite par application d'un faible voltage en courant alternatif à des électrodes inertes placées dans une solution de l'hydrocarbure en diméthylformamide.

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Spectrofluorimetric determination of microgram amounts of lead

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THE fluorescence of lead and thallium in concentrated chloride media was first reported by Pringsheim and Vogels.[1] The spectrofluorimetric determination of thallium by means of the violet fluorescence of thallium(I) in the presence of potassium chloride in concentrated hydrochloric acid has been reported.[2] Lead, copper(I), tin(II) and cerium(III) also show characteristic fluorescence emission under similar conditions, but only the lead emission is of sufficient intensity to be analytically useful. Several spot-tests have been reported for the detection of lead which exploit the formation of insoluble fluorescent complexes of lead with organic reagents.[3] This communication describes the direct determination of microgram amounts of lead by means of the violet fluorescence obtained from lead(II) under conditions similar to those used for the determination of thallium(I).[2]

viewed by a similar photomultiplier through a narrow band-pass interference monochromator, reveal that similar spectra can be recorded and calibration data obtained for 10^{-7}–$10^{-5}M$ solutions.

One of the factors which at present limits the application of electroluminescence to organic analysis is the small range of compounds which have been found to exhibit the effect. We have shown, however, that the method can be extended to the detection of aromatic amines and phenols which normally do not show significant electroluminescence, *e.g.*, 2-naphthylamine and 1-naphthol, by methylation of the deactivating group. These studies will be reported in a later communication.

Acknowledgement—We are grateful to British American Tobacco Co. Ltd., for the loan of the spectrofluorimeter used in this work.

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EXPERIMENTAL

Reagents

All the reagents used were of analytical grade. Water from an all-glass distillation apparatus was used throughout.

Lead(II) solution. A $10^{-3}M$ lead nitrate stock solution was prepared and diluted to $10^{-4}M$ as required.

Apparatus

Fluorescence measurements were made with a Farrand spectrofluorimeter fitted with 20-mμ bandwidth slits in both the exciting and analysing monochromators; no filters were used.

Calibration curve for lead

To 20 ml of saturated aqueous potassium chloride solution (*ca.* 4·1M), 30 ml of water and 30 ml of concentrated hydrochloric acid in a 100-ml volumetric flask, add accurately between 0·5 and 3·0 ml of standard $10^{-4}M$ lead(II) and dilute to volume with water. Measure the intensity of the fluorescence at 480 mμ, with an excitation wavelength of 270 mμ. The plot of fluorescence intensity against lead concentration (0·1–0·6 ppm) is a straight line which, after subtraction of the reagent blank, passes through the origin.

Prepare and measure a blank and a 0·6 ppm standard with each group of samples.

RESULTS

Spectral characteristics

Figure 1 shows the uncorrected excitation and emission spectra for the lead(II) ion in hydrochloric acid–potassium chloride solution. The correction curves appear elsewhere.[3] The excitation maximum occurs at 270 mμ and the fluorescent emission maximum at 480 mμ. Figure 2 shows the uncorrected emission spectra of more dilute solutions at much increased sensitivity with wide (20-mμ) slits and no protective filters. The peaks at approximately 550 mμ and 350 mμ are attributed to second-order diffraction from the analysing monochromator grating and stray radiation within the monochromators. The tails of these peaks make up the blank fluorescence at 480 mμ. The signal at this wavelength is directly proportional to the lead concentration, but calibration curves plotted at this level of concentration pass above the origin.

Effect of hydrochloric acid and potassium chloride concentration

The optimum hydrochloric acid and potassium chloride concentrations were found to be almost identical with those reported for the determination of thallium(I), *i.e.*, 3·3 and 0·8M respectively.

Effect of time and temperature on fluorescence

The fluorescence of a $4 \times 10^{-6}M$ lead solution prepared by the recommended procedure fell by 21% over a period of 2 hr under fluorescent tube lighting and by 20% during 2 hr of continuous irradiation at 270 mμ in the spectrofluorimeter. It is thus quite important to measure the fluorescence within 15 min of mixing the solutions.

Over the temperature range investigated, 10–40°, fluorescence intensity decreased with increase in temperature; the temperature coefficient was −1·2%/deg. All fluorescence measurements were made at 23 ± 3° by comparison with standards prepared simultaneously, so that the temperature coefficient did not invalidate the results.

Precision and accuracy

The combined chemical and instrumental precision was estimated by repetitive measurement of the fluorescence of dilute lead solutions (0·6 ppm). The standard deviation indicated an overall precision of 1% for low concentrations. Results for synthetic sample solutions are shown in Table I.

Effect of foreign ions

The effect of 31 foreign ions (added in 50-fold molar excess as 0·01M solutions) on the fluorescence of 60 μg of lead in pure solution was investigated. Ions were considered to interfere if they caused a variation of fluorescence intensity greater than ±4%. The following ions did not interfere under these conditions: Ba, Ca, Cd, Cr(III), Co, Fe(II), Hg(II), Mg, Mn(II), Ni, Ag, Sn(II), Sr, Ti(IV), Zn, citrate, fluoride, nitrate, oxalate, sulphate, sulphite, tartrate. The presence of a 50-fold excess of the following ions caused the error given in parentheses: Bi(−8%), Cr(VI)(−33%), Cu(II)(−11%), Fe(III)(−44%), Mo(VI)(−26%), Tl(I)(+100%), V(V)(−15%), ascorbic acid (−29%), metabisulphite (−34%). Attempts were made to eliminate the interferences by the use of suitable masking

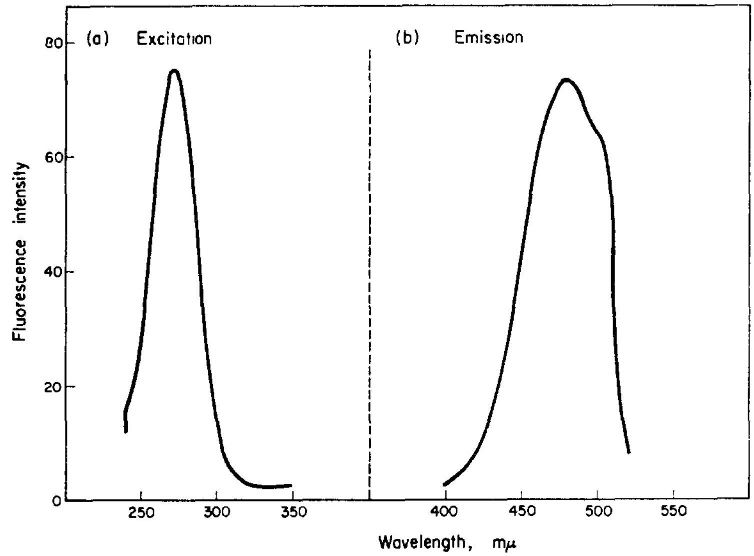

FIG. 1.—Excitation and emission spectra (uncorrected) of lead complex in HCl–KCl solution.

Lead 3·5 × $10^{-4}M$; sensitivity scale ×1.

(*a*) Excitation spectrum (emission measured at 480 mμ).

(*b*) Emission spectrum (excitation wavelength 270 mμ).

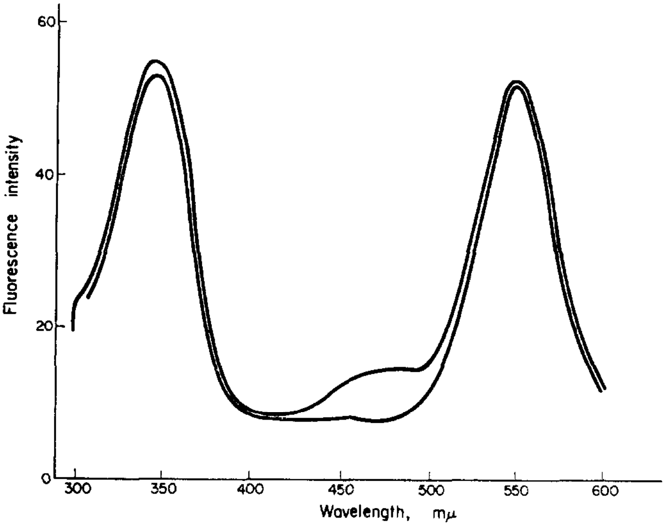

FIG. 2.—Emission spectra (uncorrected) in HCl–KCl solution for low concentrations of lead under optimum conditions.

Excitation wavelength 270 mμ; sensitivity scale ×0·1.

Top curve, Pb, $10^{-6}M$.

Bottom curve, blank.

agents. The interference of Cr(VI) was eliminated by reduction to Cr(III) by the addition of a 300-fold molar excess (relative to lead) of sulphite. The interferences from Fe(III) and V(V) were removed similarly by the addition of 100-fold and 150-fold molar excesses (relative to lead), respectively, of tin(II) chloride (0·01*M* solution) to the sample and standard solutions. Hydroxylamine, tin(II) chloride and sodium sulphite failed to eliminate the interference of copper(II) and molybdenum(VI), but a negative error of less than 4% was found to be produced when a 10-fold molar excess of copper(II), 5-fold molar excess of molybdenum(VI) or 30-fold molar excess of bismuth is present. Thallium(I) causes the most serious interference. This interference is not readily overcome by oxidation of the thallium(I) to thallium(III), and it is necessary to separate the thallium by ether extraction from hydrochloric acid as described previously.[3] Large amounts of copper may be separated from small amounts of lead by extraction of copper diethylammonium diethyldithiocarbamate from 2*M* hydrochloric acid solution into chloroform.[4]

TABLE I.—ANALYSIS OF LEAD SOLUTIONS TREATED AS UNKNOWN SAMPLES

Sample	Lead		Error, μg	Foreign ions, μg
	Present, μg	Found, μg		
1	24·9	$26{\cdot}_9$	+2	Ba (2060)
2	53·9	$53{\cdot}_9$	0·0	Mg (365)
3	45·6	$44{\cdot}_6$	−1	Sr (1314)
4	37·3	$37{\cdot}_3$	0·0	Zn (981)
5	62·2	$63{\cdot}_2$	+1	Ni (881)
6	20·7	$20{\cdot}_7$	0·0	Cd (1686)
7	49·7	$49{\cdot}_3$	$-0{\cdot}_4$	Cr(VI)(780), Mn(II)(824)
8	41·5	$43{\cdot}_5$	+2	Ni(881), Fe(III)(838)
9	62·2	$62{\cdot}_2$	0·0	Co(II)(884), Fe(III)(838)
10	53·9	$49{\cdot}_7$	−4	Co(II)(884), V(V)(764)

Discussion

The sensitivity of the procedure, although not as great as that reported for thallium, is comparable to that obtainable by spectrophotometric methods. As the fluorescence is only observed in the presence of large amounts of alkali chloride and hydrochloric acid, the usual optical procedures for elucidation of the nature of the fluorescent complex cannot be applied. The work of Pringsheim and Vogels[1] and Merritt, Hershenson and Rogers[5] suggests that the absorption spectrum observed for lead in chloride medium is characteristic of the species $PbCl_4^{2-}$, and this is most probably the species also responsible for the fluorescence emission.

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Summary—The violet fluorescence at 480 mμ of lead in concentrated hydrochloric acid–potassium chloride solution (excitation maximum 270 mμ) provides a method for the spectrofluorimetric determination of 10–60 μg of lead. The optimum conditions for the determination have been established, and the effect of 31 foreign ions examined at the 50-fold molar excess level. The interference from iron(III) and vanadium(V) is eliminated by addition of tin(II) chloride, and that of chromium(VI) by treatment with sodium sulphite.

Zusammenfassung—Die violette Fluoreszenz von Blei bei 480 nm in einer Lösung aus konzentrierter Salzsäure und Kaliumchlorid (Anregungsmaximum 270 nm) bietet eine Methode zur spektrofluorimetrischen Bestimmung von 10–60 g Blei. Die optimalen Bedingungen für die Bestimmung wurden ermittelt und der Einfluß von 31 Fremdionen bei 50-fachem molarem Überschuß untersucht. Die Störung durch Eisen(III) und Vanadium(V) wird durch Zusatz von Zinn(II)-chlorid beseitigt, die von Chrom(VI) durch Behandlung mit Natriumsulfit.

Résumé—La fluorescence violette du plomb à 480 mμ en solution acide chlorhydrique concentré-chlorure de potassium (maximum d'excitation à 270 mμ) fournit une méthode de dosage spectrofluorimétrique de 10–60 μg de plomb. On a établi les conditions optimales du dosage, et examiné les effets de 31 ions étrangers à des teneurs molaires 50 fois en excès. L'interférence du fer(III) et du vanadium(V) est éliminée par addition de chlorure d'étain(II) et celle du chrome(VI) par traitement au sulfite de sodium.

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Determination of copper in geological material by neutron activation and gamma–gamma coincidence spectrometry

THE feasibility of determining copper by activation analysis is dependent on the distribution of other elements, capable of activation, in the samples of interest. In most cases copper is present as a minor or trace element, and hence the activity of ^{64}Cu or ^{66}Cu produced by neutron activation will be shielded by activities originating from other elements present. In geological samples the most serious complication derives from ^{24}Na, formed by activation of sodium, which is usually present at the per cent level.

Thoresen,[1] using computer techniques for the analysis of gamma-spectra from soil samples, found a practical limit of detection for copper corresponding to a Na/Cu ratio of about 10^3. Schmitt *et al.*[2] determined amounts of copper of 30–170 ppm in meteorites with a sodium content of 0·2–0·6%, using the peak area ratio 0·51 MeV/2·75 MeV in the gamma-spectrum of a ^{24}Na-standard to correct for the contribution of ^{24}Na to the 0·51-MeV annihilation peak of ^{64}Cu in the gamma spectra of the meteorite samples.

Application of a Ge(Li) detector has been reported in the case of a sulphide ore,[3] where the ^{24}Na content was too low to cause any serious interference.

The fact that ^{64}Cu is one of the very few positron-emitting nuclides produced by thermal neutron activation has led several investigators to take advantage of the 180° annihilation quanta for gamma-gamma coincidence measurements. In this manner the detection rate of ^{64}Cu as compared to most other activities is greatly enhanced. The use of this principle for the determination of copper by neutron activation was first mentioned by Ljunggren,[1] who proposed applications to biological materials. More recent investigations have included determinations of amounts of copper in beryllium,[5] iron,[6] and bismuth[7] in the ppm range. Gorski *et al.*[8] employed a similar technique for the determination of copper in ores, using 14-MeV neutrons and measuring the activity of the 9·8 min positron emitter ^{62}Cu, produced by $(n, 2n)$ reactions. This technique, however, does not seem to be applicable to samples containing only trace amounts of copper, as some of the major elements in rocks also form β^+-emitters by 14-MeV neutron activation.

The gamma-gamma coincidence technique should be suitable for increasing the sensitivity of copper determinations in the presence of a large excess of ^{24}Na, since the annihilation of all β^+-particles from ^{64}Cu can be made to occur close to the sample position, and hence can be detected with a reasonable probability by coincidence detectors placed in opposite directions, while the pair production process of ^{24}Na is most likely to take place somewhere else in the system, thus giving a very minute probability of 180° coincidence detection. In the present work applications of such a technique for the copper determination in some geological samples are shown.

EXPERIMENTAL

Instrumentation

The detectors used for the measurements were Harshaw integral line detectors with 2 × 2 in. NaI(Tl) crystals directly attached to RCA 6342 A photomultiplier tubes The detectors were connected

Résumé—La fluorescence violette du plomb à 480 mμ en solution acide chlorhydrique concentré-chlorure de potassium (maximum d'excitation à 270 mμ) fournit une méthode de dosage spectrofluorimétrique de 10–60 μg de plomb. On a établi les conditions optimales du dosage, et examiné les effets de 31 ions étrangers à des teneurs molaires 50 fois en excès. L'interférence du fer(III) et du vanadium(V) est éliminée par addition de chlorure d'étain(II) et celle du chrome(VI) par traitement au sulfite de sodium.

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EXPERIMENTAL

Instrumentation

The detectors used for the measurements were Harshaw integral line detectors with 2 × 2 in. NaI(Tl) crystals directly attached to RCA 6342 A photomultiplier tubes The detectors were connected to Hamner charge-sensitive preamplifiers and linear amplifiers capable of delivering either a symmetrical double-delay line or a single-delay line output pulse. From the linear amplifiers the pulses were fed to Hamner jitter-free pulse-height analysers which were coupled to a fast coincidence unit with a variable resolving time in the range 10–150 nsec. The timing of each single channel pulse analyser was adjustable over a range of 200 nsec, and accidental coincidence rates were evaluated by introducing a fixed delay of 0·5 μsec in one channel. The output of the coincidence unit was used to gate a Tullamore transistorized 400-channel pulse-height analyser which was used for pulse analyses of the spectrum from one detector. The spectrum recorded by the analyser could be printed out on a Monroe data printer.

Samples and standards

The samples selected for this investigation were five different qualities of iron ore (I–V) and two samples of silicate rocks, *i.e.*, an amphibolite (VI) and a diabase (W-1). The standard rock W-1, issued by the U.S. Geological Survey, was included to check the accuracy of the method.

The standard rock "Sulphide ore-1" from the Canadian Association for Applied Spectroscopy was selected as standard. This rock has a copper content of 8300 ppm,[9] and a sodium content of 0·70%. The value 8300 ppm, which is the mean value of analyses mainly based on chemical and emission spectrographic techniques, was checked with radiochemical activation analysis according to the method of Brunfelt *et al.*[10] and agreement was found within experimental error. To correct for the contribution of ^{24}Na in the measurements, it was also necessary to have a sodium standard. The standard rock STM-1 from the U.S. Geological Survey, with a sodium content[11] of 6·1% and a copper content[10] as low as 2·0 ppm was chosen for this purpose.

Procedure

Finely crushed samples (about 300 mg) were transferred to small polyethylene vials and irradiated for 30 min at a thermal neutron flux of $2{\cdot}5 \times 10^{12}$ n.cm^{-2}.sec^{-1} in the JEEP-I reactor (Kjeller, Norway). After the activation the samples were allowed to stand for 24 hr, for the decay of the ^{56}Mn activity. Portions of 50–100 mg of the irradiated samples were then weighed into flat-bottomed polyethylene tubes of 6·0 mm inner diameter. For STM-1 a sample size of 20 mg was used, otherwise the ^{24}Na activity induced would have been too strong.

For the gamma-activity measurements the tubes were mounted in a perspex sample holder placed in the central axis of the detectors, which were kept at an angle of 180° relative to each other. The distance between the sample and the detectors was so adjusted that the dead time of the analyser in no case exceeded 40% when the detector pulses were fed *via* the preamplifier directly into the multichannel analyser.

In the coincidence measurements a counting period of 5–20 min was employed, depending on the amount of copper in the sample. The total gamma-spectra of the samples were also recorded to measure the sodium content of the samples through the 1·37-MeV photopeak of ^{24}Na. By means of these sodium values and of the coincidence counting rate of the sodium standard STM-1, correction could be made for the ^{24}Na contribution of the 0·511-MeV peak in the gamma-gamma coincidence measurements.

The sodium content of the copper standard corresponded to a correction of 0·25%. On the other hand, the copper content of the sodium standard contributed to 1·0% of the 0·511-MeV coincidence peak. The areas of the photopeaks were evaluated according to the method of Covell.[12]

In Fig. 1 the effect of applying the coincidence principle as compared to a direct measurement is illustrated for sample IV in Table I.

RESULTS AND DISCUSSION

The results obtained for each of the seven samples, together with the mean values, are given in Table I. The relative standard deviation of a single value has been calculated for each sample, and is in the range 1·9–6·4%. In the table data are also included demonstrating the effect of the ^{24}Na interference at various Na/Cu abundance ratios.

To get an estimate of the reliability of the method for samples with a high Na/Cu ratio, sample VI was analysed by radiochemical activation, using the method of Brunfelt *et al.* The results of this investigation are given in Table II, and show very good agreement with the gamma–gamma coincidence results. The present result for W-1 is also in agreement with the previous neutron-activation values quoted in the table. Good agreement is also found with the recommended value of 110 ppm given by Fleischer.[17] This value is based on emission spectrographic and colorimetric data.

The spread of replicate determinations in this work is due to counting errors and errors due to neutron flux inhomogeneity in the irradiation position. Neutron-shielding effects are not expected to affect the present results seriously, since no strong neutron-absorbing elements are present in

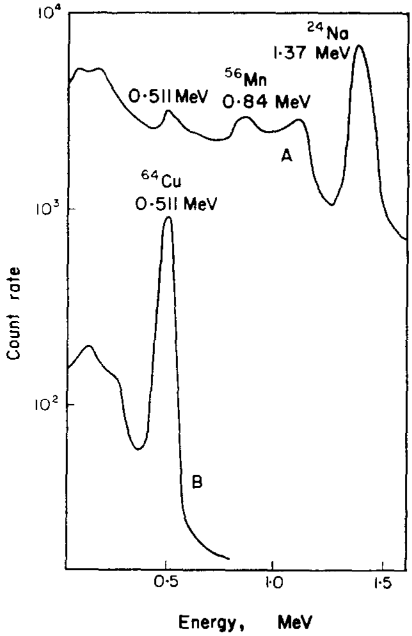

FIG. 1.—Single and coincidence gamma-spectra of sample IV (Table I) recorded one day after irradiation.
A: Single spectrum—2-min counting time
B: Coincidence spectrum—10-min counting time

TABLE I.—COPPER CONTENT OF SOME GEOLOGICAL SAMPLES DETERMINED BY NEUTRON ACTIVATION AND GAMMA–GAMMA COINCIDENCE SPECTROMETRY

Sample	I	II	III	IV	V	VI	W-1
Cu-content *ppm*	665 634 636 661 632	371 384 376 389 381	317 307 314 315 301	250 284 242 243 255	224 231 213 218 204	61 57 63 57 56	116 118 116 112 115
Mean, *ppm*	646	380	311	255	218	59	115
Relative standard deviation of single value, %	2·5	1·9	2·1	6·4	4·7	5·2	2·0
Na-content, %	0·213	0·170	0·260	0·70	0·84	1·95	1·50
Na/Cu	3·3	4·5	8·4	27	39	330	130
Fraction of 0·511-*MeV* photopeak due to ^{24}Na %	1·0	1·4	2·5	7·5	11·0	49	26·5

appreciable amounts in the samples. Possible interference from the nuclear reaction ^{64}Zn(n, p)^{64}Cu might be significant, but becomes important only if the zinc content is 100 times higher than the copper content. As no serious systematic errors seem to influence the results, and as the agreement with results obtained by other techniques is good, the error of the present method is probably of the order of ±5%, even for the silicate rock samples.

TABLE II.—COMPARISON OF THE GAMMA–GAMMA COINCIDENCE DATA FOR Cu IN SAMPLES VI AND W-1 WITH RESULTS OBTAINED BY OTHER METHODS

Sample	Present work		Previous values	
	Gamma–gamma coincidence	Radiochemical	Neutron activation (reference)	Recommended value
VI	59	56, 57, 59, 54 mean 57	—	—
W-1	115	—	116 (10) 112 (13) 120 (14) 110 (15) 116 (16)	110

CONCLUSION

The present neutron activation method based on gamma-gamma coincidence measurements should facilitate rapid and accurate measurements of copper in the concentration region 0·01–0·1%. In this region the conventional type of instrumental activation analysis usually becomes difficult owing to the contribution from ^{24}Na to the gamma-spectrum. It is also possible to get good results at lower copper concentrations, but long counting periods are necessary to obtain satisfactory counting statistics. For sodium-rich rocks with copper contents at the ppm level, methods based on rapid radiochemical separation would therefore be preferable.

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Summary—The copper content of some geological samples has been determined by thermal neutron activation and subsequent coincidence gamma-spectrometry, taking advantage of the 180° annihilation quanta of ^{64}Cu. By this means the interference of ^{24}Na, which is often the major gamma-activity induced in geological materials, is greatly reduced. The method is precise to about ±5%, and the error is of the same order. The method should be especially attractive for application to samples with a copper content of 100–1000 ppm.

Zusammenfassung—Der Kupfergehalt einiger geologischer Proben wurde durch Aktivierung mit thermischen Neutronen und anschließende Koinzidenz-Gammaspektometrie bestimmt, wobei die 180°-Vernichtungsquanten von ^{64}Cu ausgenutzt wurden. Auf diese Weise wird die Störung durch ^{24}Na, das oft den Großteil der in geologischem Material induzierten Gamma-Aktivität darstellt, stark reduziert. Die Methode ist auf etwa ±5% genau, der Fehler liegt in der gleichen Größenordnung. Die Methode sollte besonders zur Anwendung auf Proben mit Kupfergehalten von 100–1000 ppm vorteilhaft sein.

Résumé—On a déterminé la teneur en cuivre de quelques échantillons géologiques par activation de neutrons thermique suivie de spectrométrie de coïncidence gamma, tirant avantage de l'annihilation 180° des quanta de ^{64}Cu. De cette manière, l'interférence de ^{24}Na, qui est souvent la principale activité gamma induite dans les matériaux géologiques, est fortement réduite. La méthode est précise à environ ±5% et l'erreur est du même ordre. La méthode devrait être particulièrement intéressante pour son application à des échantillons à teneur en cuivre de 100–1000 p.p.m.

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Kinetic titration with differential thermometric determination of the end-point

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THERMOMETRIC end-point determination has been used so far in the titration of solutions with minimum concentrations of 10^{-3}–$10^{-4}M$. The temperature changes occurring in the titration of solutions more dilute than this cannot be separated with sufficient clarity from the background changes stemming from various sources (heat conduction, evaporation, temperature differences inside the system, heat of dilution, heat of dissociation, *etc.*). In the past few years we have been able to lower this concentration limit by the introduction of catalytic reactions,[1,2] and now describe a differential thermometric method of end-point detection.

The velocity of homogeneous catalytic reactions is proportional to the concentration of the catalyst and to some function of the concentrations of the other reacting substances. In two solutions identical except that catalyst is absent from one of them (reference solution), the reaction velocities can be made identical if the reference solution is titrated with a dilute ($10^{-3}M$) solution of catalyst until the catalyst concentration in both solutions becomes the same. The titration can be monitored by measuring the difference in the rates of change of temperature in the two solutions by means of thermistors in a Wheatstone bridge circuit; the rates becoming equal at the end-point. If an excess of titrant has been added the end-point may be established by back-titration of the sample solution with catalyst.

If the temperature change is not too great, its rate will be related to the rate of reaction through the heat of reaction:

$$dT/dt = k \, . \, dc/dt \qquad (1)$$

Résumé—On a déterminé la teneur en cuivre de quelques échantillons géologiques par activation de neutrons thermique suivie de spectrométrie de coïncidence gamma, tirant avantage de l'annihilation 180° des quanta de ^{64}Cu. De cette manière, l'interférence de ^{24}Na, qui est souvent la principale activité gamma induite dans les matériaux géologiques, est fortement réduite. La méthode est précise à environ $\pm 5\%$ et l'erreur est du même ordre. La méthode devrait être particulièrement intéressante pour son application à des échantillons à teneur en cuivre de 100–1000 p.p.m.

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If the temperature change is not too great, its rate will be related to the rate of reaction through the heat of reaction:

$$dT/dt = k \,.\, dc/dt \tag{1}$$

where dT/dt is the rate of change of temperature, k is a proportionality constant and dc/dt is the rate of reaction. The rate of reaction is proportional to the concentration of catalyst present. If the heat of reaction is substantial, dT/dt may be measured conveniently and is one of the simplest means of following the course of reaction velocity.

These considerations are not, however, valid for all types of catalytic reactions, and even when they are, some stipulations must be made about the experimental conditions and the reactions which may be used. The initial temperatures of the sample and reference solutions must be identical since the rates of catalytic reactions are strongly temperature dependent. The concentration of the catalyst in the sample solution must be adjusted so that the rate of change of temperature is 0·01–0·1°/min; such a rate may be measured easily and will not cause a significant difference in the temperatures of the sample and reference solutions in the course of the titration. Catalytic reactions with long induction periods are generally unsuitable; in such cases the relationships above are valid only if the catalyst concentration is identical in both solutions at the start of the reaction.

Reactions with induction periods may be used for kinetic titration with thermometric end-point determination only if the induction period is short (less than 1 sec), and the titrant contains the catalyst in the post-induction state so that the induction period for the reference solution is eliminated. Autocatalytic reactions are not suitable, because the concentration of the active catalyst molecules increases continuously with time.

The reaction velocity should remain practically constant in the sample solution during titration; this may be realized chiefly by using high concentrations of the substrates, so that these concentrations remain almost constant. The situation is less favourable if the reaction velocity is proportional to a higher power of the substrate concentrations, since it will be altered by minor concentration variations.

In a favourable case the catalyst reacts in a fast step with substrate A to form an intermediate which then reacts in a slower step with substrate B to release the catalyst; the reaction velocity then depends chiefly on the concentration of B and it is sufficient to keep this constant.

The volume change during titration should be as small as possible. If it is large the attendant variation of concentration and heat capacity may be compensated by diluting the sample solution with distilled water to the same extent.

The suitability of catalytic reactions should be investigated before they are used for kinetic titrations.

EXPERIMENTAL

Apparatus

The equipment used is practically the same as that used by Keily and Hume[3] and is shown in Fig. 1.

The rate of change of temperature is measured by two thermistors built into two separate Wheatstone bridges which may be connected in opposition (Fig. 2). A galvanometer is used as sensing instrument. The range of measurement is adjusted over wide limits by the use of shunts. At the start, when the reaction velocities of the sample and reference solutions differ rather widely, low sensitivity is used and as the reaction velocities approach each other the sensitivity is increased to the maximum (1 scale division of the Zeiss galvanometer used is equal to 0·0001°).

Determination of cobalt

The practical application of the method is illustrated by the determination of cobalt in concentrations below $10^{-4}M$.

Cobalt catalyses the oxidation of tartaric acid by hydrogen peroxide. Preliminary experiments showed that if the tartaric acid concentration is sufficiently high, the rate of oxidation catalysed by cobalt ions may be regarded as constant for 3 min, which is amply sufficient for performing the titration.[3]

Standard cobalt solution, 0·0001M. Add 30 ml of 50% tartaric acid solution, 350 ml of water and 75 ml of 30% sodium hydroxide solution to 10 ml of 0·05M cobalt solution. Cool the mixture and add 10 ml of 30% hydrogen peroxide. After decomposition of the peroxide (1–2 min) cool the solution and dilute it to 500 ml in a standard flask to obtain the titrant solution containing cobalt in its catalytically active oxidation state. The solution is stable for about a week.

Procedure. Add 2 ml of hydrochloric acid (1 + 1) to a solution containing 0·03–0·3 mg of cobalt and evaporate it to dryness. Dissolve the residue in 5 ml of hydrochloric acid (1 + 1), add 10 ml of 50% tartaric acid and 50 ml of distilled water, neutralize with 30% sodium hydroxide solution and add 20 ml in excess. Cool and dilute the solution to 200 ml. Prepare a reference solution of the same composition except for the cobalt. Bring both solutions to room temperature, transfer them to the Dewar flasks, insert the stirrers and thermistors, compensate the Wheatstone bridges separately and connect them in opposition. Add 5 ml of 30% hydrogen peroxide to both solutions at the same time

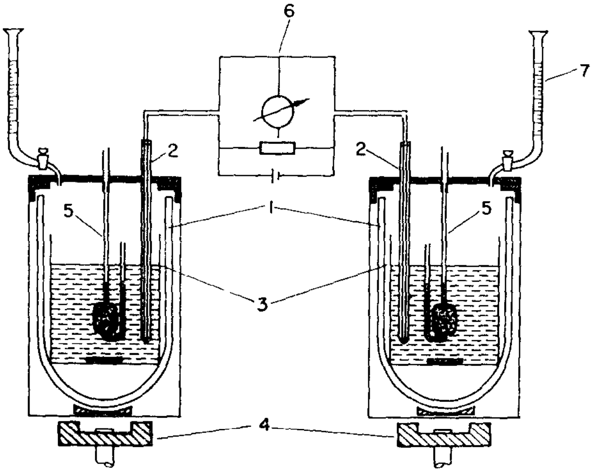

FIG. 1.—Sketch of the apparatus.
1—Dewar vessel; *2*—thermistor; *3*—plastic beaker; *4*—magnetic stirrer; *5*—dip pipette; *6*—Wheatstone bridge; *7*—burette filled with 0·001*M* cobalt solution.

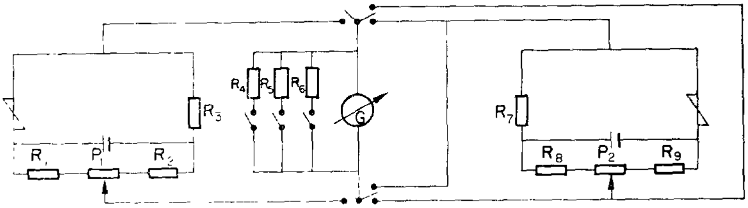

FIG. 2.—Sketch of opposing Wheatstone bridges.
Details of values of resistors *etc.* are not shown but may be obtained from the author.

to start the reaction, and titrate the reference solution with the standard cobalt solution until the pointer of the sensing instrument comes to rest, using minimum sensitivity initially and maximum sensitivity at the end.

Nickel ions slightly inhibit the reaction but titration is possible in their presence if the reference solution contains the same amount of nickel salt as the sample solution. The nickel salt added to the reference solution must be free from cobalt, and may be prepared by passing a solution of nickel chloride in $9M$ hydrochloric acid through a strongly basic anion-exchanger (*e.g.*, Dowex 1) and removing the excess of acid by evaporation. To determine cobalt in nickel, dissolve 1 g of sample in nitric acid (1 + 1) and evaporate it to dryness. Dissolve the residue in 25 ml of hydrochloric acid (1 + 1) with slow heating and dilute to 100 ml in a standard flask. Take 20 ml of this solution, add 15 ml of 50% tartaric acid and 50 ml of water, and then neutralize and proceed as described before, using a reference solution containing cobalt-free nickel.

TABLE I.—RESULTS FOR VARIOUS CONCENTRATIONS OF COBALT

[Co], *M*	Cobalt taken, μg	Co found, μg
5×10^{-7}	5·9	7·1
1×10^{-6}	11·8	12·4
$2{\cdot}5 \times 10^{-6}$	29·4	30·6
5×10^{-6}	59	62
1×10^{-5}	118	119
$2{\cdot}5 \times 10^{-5}$	294	306

TABLE II.—COBALT IN NICKEL

Sample	Co, %	
	photometric	kinetic titration
3215	0·008	0·01
3214	0·009	0·007
4732	0·07	0·08
4947	0·08	0·09
2185	0·23	0·27
6417	0·27	0·29

Typical results are shown in Tables I and II.

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Summary—A method has been described for the determination of concentrations below $10^{-4}M$ by applying catalytic reactions and using thermometric end-point determination. A reference solution, identical with the sample solution except for catalyst, is titrated with catalyst solution until the rates of reaction become the same, as shown by a null deflection on a galvanometer connected *via* bridge circuits to two opposed thermistors placed in the solutions.

Zusammenfassung—Eine Methode zur Bestimmung von Konzentrationen unter $10^{-4}M$ mit Hilfe katalytischer Reaktionen und thermometrischer Endpunktsanzeige wird beschrieben. Eine mit der Probelösung bis auf die Abwesenheit des Katalysators identische Lösung wird mit Katalysator titriert, bis die Reaktionsgeschwindigkeiten gleich werden. Dies wird durch den Ausschlag Null auf einem Galvanometer angezeigt, das in Brückenschaltung an zwei gegeneinander geschaltete Thermistoren in den Lösungen angeschlossen ist.

Résumé—On décrit une méthode pour le dosage de concentrations inférieures à $10^{-4}M$ par application de réactions catalytiques et en utilisant une détermination thermométrique du point de fin de dosage. Une solution de référence, identique à la solution échantillon à l'exception du catalyseur, est titrée par la solution de catalyseur jusqu'à ce que les vitesses de réaction deviennent les mêmes, comme le montre la déviation nulle d'un galvanomètre relié par l'intermédiaire de circuits en pont à deux thermistors en opposition placés dans les solutions.

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POLAROGRAPHIC STUDY OF COMPLEXES OF METAL IONS AND DIBASIC ACIDS—II

COMPLEXES OF LEAD WITH MALONIC, SUCCINIC, GLUTARIC AND ADIPIC ACIDS

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Summary—The malonate, succinate, glutarate and adipate complexes of lead have been examined polarographically and the overall stability constants evaluated. The values found are log $\beta_1 = 2{\cdot}60$, 2·40, 2·48, 2·38; log $\beta_2 = 3{\cdot}62$, 3·73, 3·45, 3·20; log $\beta_3 = 4{\cdot}32$, 4·11, 3·90, 3·69, for the malonate, succinate, glutarate and adipate complexes respectively.

The polarographic behaviour of the complexes of lead with formic acid and tartaric acid has been studied by Hershenson[1] and Iwase[2] respectively. The complexes of lead with oxalic acid,[3] salicylic acid,[4] glutamic acid[5] and glycollic acid[6] have been investigated polarographically. In a study of the polarography of lead in the presence of various complexing agents it was found that lead is reduced reversibly in a malonate, succinate, glutarate and adipate media and the reduction is diffusion controlled.

The present paper deals with the determination of the composition and stability constants of the complexes formed by lead with malonate, succinate, glutarate and adipate.

EXPERIMENTAL

Reagent grade chemicals were used. The $0{\cdot}001M$ solution of lead was prepared from lead nitrate. Sodium perchlorate was used to keep the ionic strength constant at 2·0. Solutions of the sodium salts of malonic, succinic, glutaric and adipic acids were prepared by adding sodium hydroxide to the respective acids and adjusting the pH to approximately 6·5.

An L.P. 55 Heyrovský manual polarograph was used. The dropping mercury electrode had the following characteristics: $m = 2{\cdot}12$ mg/sec; $t = 4{\cdot}2$ sec (at $-1{\cdot}0$ V *vs.* S.C.E. in $0{\cdot}1M$ sodium perchlorate). A constant temperature of 30 ± 0·01° was maintained by means of a Haake-type ultrathermostat. All the half-wave potentials were measured with a saturated calomel electrode as reference. Triton X-100 was used as maximum suppressor. All the polarograms were recorded after deaeration of the test solutions with purified nitrogen.

THEORY

It has been shown by DeFord and Hume[8] that the shift in half-wave potential due to complex formation can be expressed as:

$$\Delta E_{1/2} = (E_{1/2})_c - (E_{1/2})_s = \frac{2{\cdot}303RT}{nF} \log_{10} \gamma_M \frac{I_c}{I_s} \sum_0^N \frac{\beta_j\{X\}^j}{Y_{MX_j}} \tag{1}$$

where $(E_{1/2})_c$ and $(E_{1/2})_s$ are the half-wave potentials of the complex and simple metal ions respectively, R, T and F have their usual significance, n denotes the number

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of electrons involved in the reduction, I_s and I_c are the experimental diffusion currents for the simple and complex ions respectively, β_j is the overall formation constant of the the jth complex; $\{X\}$ is the activity of the complexing ligand and γ_M and γ_{MX_j} denote the activity coefficients, at the electrode surface, of the metal and complex species respectively. Equation (1) can be rearranged to define a function $F_0([X])$:

$$F_0([X]) = \text{antilog}_{10}\left[\frac{0\cdot4343nF}{RT}\,\Delta E_{1/2} + \log\frac{I_s}{I_c}\right] = \gamma_M \sum_0^N \frac{\beta_j[X]^j}{\gamma_{MX_j}}$$

$$= 1 + \beta_1[X]\frac{\gamma_M\gamma_X}{\gamma_{MX}} + \beta_2[X]^2\frac{\gamma_M(\gamma_X)^2}{\gamma_{MX_2}} + \ldots \quad (2)$$

Equation (2) can be written in the forms (3), (4) and (5) if the ionic strength is kept constant and the activity coefficients are taken as also being constant:

$$F_1([X]) = \{F_0([X]) - 1\}/[X] = \beta_1 + \beta_2[X] + \beta_3[X]^2 + \ldots \quad (3)$$

$$F_2([X]) = \{F_1([X]) - \beta_1\}/[X] = \beta_2 + \beta_3[X] + \ldots \quad (4)$$

$$F_3([X]) = \{F_2(X) - \beta_2\}/[X] = \beta_3 + \beta_4[X] + \ldots \quad (5)$$

where [X] denotes the concentration of the complexing ligand, and γ the activity coefficient of the species indicated by subscript. β_1, β_2 and β_3 are the overall formation constants for the complexes containing one, two and three ligands respectively. Values of $F_0([X])$ for various concentrations of the complexing ligand can be determined experimentally and equation (2) can then be solved graphically for β_1, β_2 and β_3.

The proportion of the uncomplexed metal ion and the various complex species as a function of the ligand concentration can be calculated by means of the equations

$$\frac{M}{C_M} = \frac{1}{F_0([X])} \quad (6)$$

$$\frac{MX_j}{C_M} = \frac{\beta_j[X]^j}{F_0([X])} \quad (7)$$

where M denotes the concentration of uncomplexed metal ions, MX_j is the concentration of the jth complex and C_M is the total concentration metal ion added to the system.

RESULTS AND DISCUSSION

In each case, a single well-defined reduction wave appeared. The half-wave potential was found to shift towards more negative value with increasing concentration of ligand (malonate, succinate, glutarate and adipate). The plots of i_d *vs.* $\sqrt{h}$ and i_d *vs.* [Pb^{2+}] were found to be straight lines passing through the origin, showing that the reduction is diffusion controlled (i_d is the diffusion current, h the head of mercury). The diffusion current was found to decrease with increase in ligand concentration, which may be due to the change in the size of the particle resulting from complex formation. The complex ions formed are much larger than the aquo-ion, hence the lower value of the diffusion current with increase in ligand concentration.

The plots of $\log i/(i_d - i)$ *vs.* E were found to be linear with a slope of the order of 31 ± 2 mV, indicating the reversibility of the reduction. The value of n was 2.

The plots of $E_{1/2}$ *vs.* $-\log C_X$ (where C_X is the total ligand concentration) were found to be a smooth curve (Fig. 1), showing the formation of two or more complex species which are in equilibrium. The classical method due to Lingane[7] could not be applied, and the DeFord and Hume treatment[8] as modified by Irving[9] was applied.

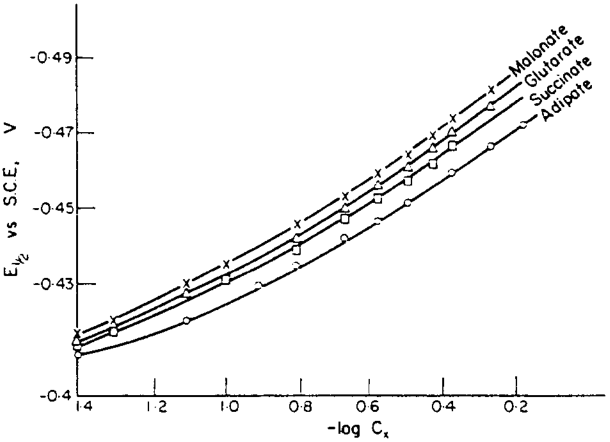

FIG. 1.—Plots of $E_{1/2}$ *vs.* $-\log C_X$.

The values of the over-all formation constants, β_j, were calculated by the graphical extrapolation method Figs. 2–5. The presence of three complex species Pb(A), $Pb(A)_2^{2-}$ and $Pb(A)_3^{4-}$ was established where A stands for malonate, succinate, glutarate or adipate, as the case may be. The formation constants i.e., β_1, β_2 and β_3 are given in Table I, and are larger than the corresponding values for Cd^{2+},[10] which is usually the case.

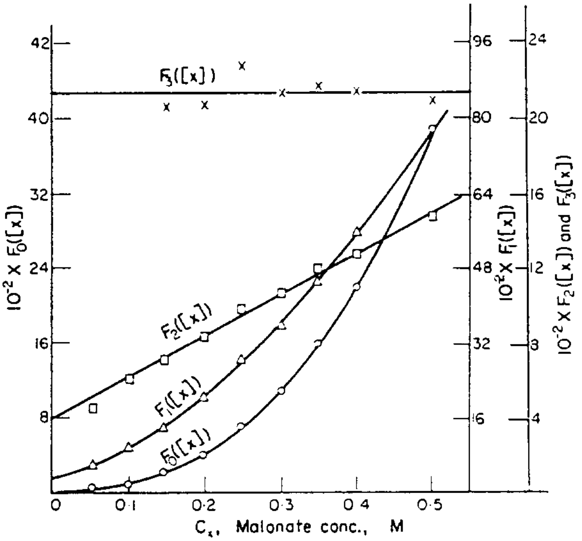

FIG. 2.—Plots of $F_j([X])$ for lead-malonate system.

The distribution of lead present in various forms was calculated as a function of the logarithm of the ligand concentration by means of equatons (6) and (7). The results are shown in Figs. 6 and 7.

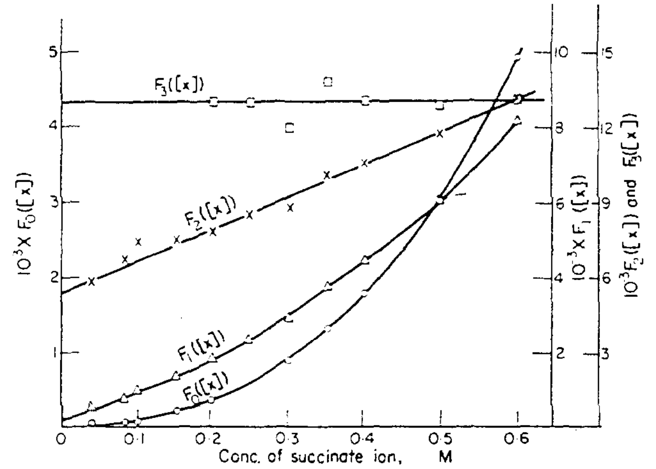

FIG. 3.—Plots of F_j([X]) for lead-succinate system.

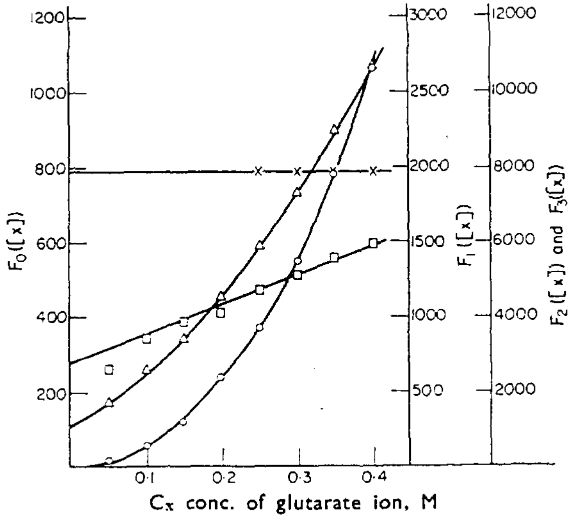

FIG. 4.—Plots of F_j([X]) for lead-glutarate system.

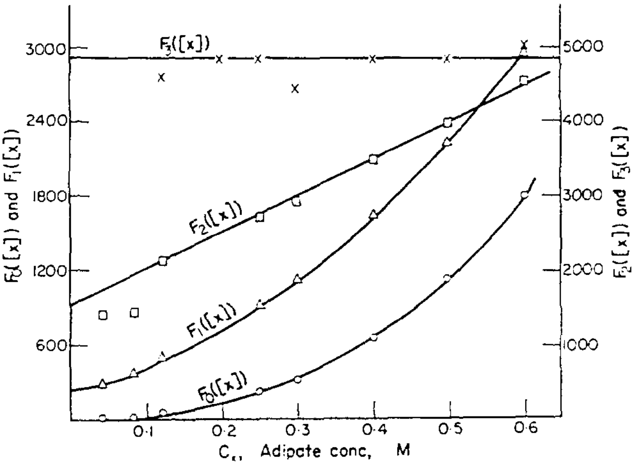

FIG. 5.—Plots of F_j([X]) for lead-adipate system.

TABLE I.—OVER-ALL FORMATION CONSTANTS OF LEAD COMPLEXES WITH VARIOUS DIBASIC ACIDS

Complexing agent	β_1	β_2	β_3
Malonate	$4{\cdot}0 \times 10^2$	$4{\cdot}2 \times 10^3$	$2{\cdot}1 \times 10^4$
Succinate	$2{\cdot}5 \times 10^2$	$5{\cdot}4 \times 10^3$	$1{\cdot}3 \times 10^4$
Glutarate	$3{\cdot}0 \times 10^2$	$2{\cdot}8 \times 10^3$	$7{\cdot}9 \times 10^3$
Adipate	$2{\cdot}4 \times 10^2$	$1{\cdot}6 \times 10^3$	$4{\cdot}9 \times 10^3$

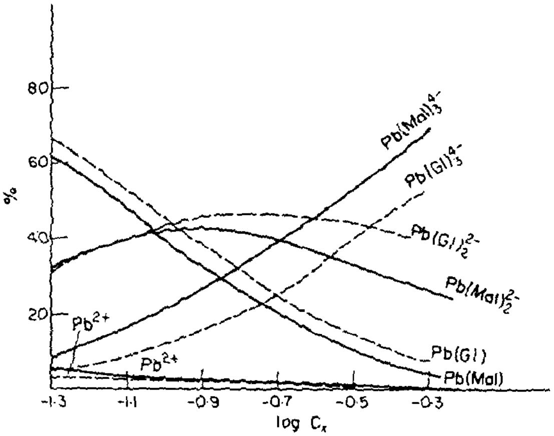

FIG. 6.—Distribution diagrams for lead malonate and glutarate systems.

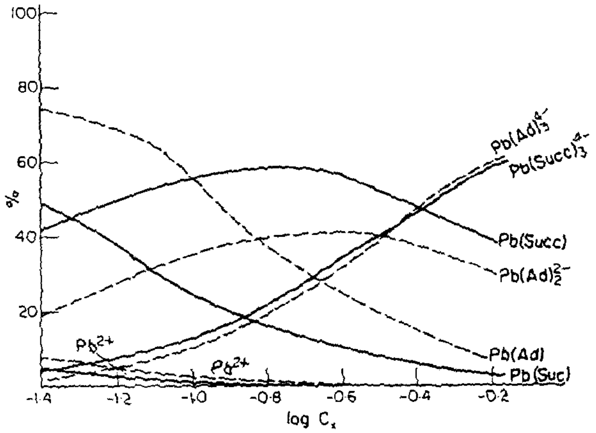

FIG. 7.—Distribution diagrams for lead succinate and adipate systems.

As the reduction of lead is diffusion controlled, lead can be estimated polarographically in malonate, succinate, glutarate and adipate solutions.

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Zusammenfassung—Die Komplexe von Blei mit Malonat, Succinat, Glutarat und Adipat wurden polarographisch untersucht und die Gesamtstabilitätskonstanten ermittelt. Es wurden gerfunder $\log \beta_1 =$ 2,60; 2,40; 2,48; 2,38; $\log \beta_2 =$ 3,62; 3,73; 3,45; 3,20; $\log \beta_3 =$ 4,32; 4,11; 3,90; 3,69 für die Komplexe in obiger Reihenfolge.

Résumé—On a examiné polarographiquement les complexes malonique, succinique, glutarique et adipique du plomb et évalué toutes les constantes de stabilité. Les valeurs trouvées sont $\log \beta_1 =$ 2,60; 2,40 2,48; 2,38; $\log \beta_2 =$ 3,62; 3,73; 3,45; 3,20; $\log \beta_3 =$ 4,32; 4,11; 3,90; 3,69, pour les complexes malonique, succinique, glutarique et adipique respectivement.

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SUBSTOICHIOMETRIC MASKING—I

GENERAL CONSIDERATIONS AND QUANTITATIVE TREATMENT

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Summary—Substoichiometric masking is effected by adding a masking agent in an amount less than that equivalent to the substance to be masked. The amount of free interfering substance is thereby to be reduced below the interference threshold, that is, the level at which interference occurs. The approach is advantageous in cases where the available masking agents when added in excess profoundly affect the substance to be determined. Formulae to evaluate the feasibility of substoichiometric masking are derived and a general discussion of the situation is given.

THE selectivity of reagents and reactions has always been a point of great concern in analytical chemistry. Presently, much emphasis is being placed on cases in which small amounts of one component of a sample have to be detected or determined in the presence of large amounts of other components. Since most separation procedures are difficult or impractical in such cases, the problem of selectivity has become of crucial importance. The number of sufficiently selective reagents available at the present time is limited, as is the probability of finding new ones. Therefore, considerable effort has been, and is being, expended in order to improve the selectivity of tests and determinations through the use of masking techniques. Of course the problem of selectivity also exists with respect to masking reagents, but with appropriate combinations of test and masking reagents, many problems have been solved, and, in some cases, rather spectacular results have been achieved.

The usual procedure for applying a masking reagent is to add it in an amount which is at least equivalent to that of the substance to be masked; but, for obvious reasons, an excess is commonly employed. This excess often has a detrimental effect on the principal reaction and then any increase in selectivity is offset by a considerable decrease in sensitivity. A possible masking technique which, to the best of our knowledge, has not yet been studied and applied, involves the addition of an amount of masking reagent less than that equivalent to the substance to be masked . The general and quantitative aspects of such a technique will be discussed in the present paper.

SUBSTOICHIOMETRIC MASKING

Suppose a metal N is to be determined (or detected) in the presence of a metal M. Interference, in general, will only occur if metal M is present above a certain level. This level may be termed the "interference threshold" (German "Störschwelle"). Two cases may be differentiated. First, the absolute amount or concentration of metal M is essentially the decisive factor and an "absolute interference threshold" may be defined. As an example, a case may be considered where metal M imparts an intense colour to the solution and thus impairs the sharpness of the end-point in a titration.

Second, and more frequently, the amount or concentration of the interfering metal relative to that of the metal to be determined is the critical factor; then the "relative interference threshold" becomes of interest. For example, the interfering metal M is partially co-titrated; then the relative error introduced into the result for metal N will depend on the ratio of the amounts of the two metals. Situations where the relative thresholds are of critical significance are more frequent and commonly more difficult to handle. Such cases are of greater practical importance and will be dealt with in the present paper.

As long as the ratio of C_M/C_N (where C denotes the analytical concentration) is below the interference threshold no problem exists. If this threshold value is exceeded the interference becomes increasingly serious and the determination may even be rendered completely impossible. In such a case, the addition of a masking reagent in an amount less than that equivalent to the metal M but just sufficient to reduce the concentration ratio [free M]$/C_N$ below the threshold value might be advantageous. Such a procedure would be termed "substoichiometric masking." The term "partial masking" might *per se* be considered as equally appropriate, but use of this term could lead to confusion, since phrases like ". . . element X is partially masked" do not imply, according to present terminology, that a substoichiometric amount of masking reagent is added. "Partial masking" commonly refers to a situation in which an excess of masking reagent has been added, and the reaction of the interfering substance, although diminished in extent, is not completely but only partially suppressed. Further, it should be emphasized that the terms "interference" and "masking," as used here, are not restricted to chemical phenomena but are used in the broader sense of causing and eliminating, respectively, detrimental effects of all sorts. Thus, undesirable instrumental response may be included in these terms as may be seen from the following example.

The polarographic analysis of a cadmium–zinc sample proceeds quite uneventfully if small amounts of cadmium are to be determined in the presence of large amounts of zinc. The situation is favourable because in most practical supporting electrolytes the cadmium wave precedes the zinc wave sufficiently to allow the measurement of the diffusion current of the cadmium without any interference from zinc even though this element is present in a considerable amount. However, in the opposite case, a small zinc wave rides on top of a huge cadmium wave and the diffusion current of the zinc can be evaluated only with great difficulty. Here, substoichiometric masking would be very useful and would be achieved by the addition of a complexing reagent which, under the prevailing conditions, complexes preferentially with the cadmium. The major portion of the cadmium would then be present as a complex that does not yield a polarographic wave in the potential range concerned. The polarographic wave due to the small amount of uncomplexed cadmium would not interfere with the evaluation of the diffusion current of the zinc. In order to test this idea, several chelons were tried and satisfactory results were obtained with many of them. Obviously each of these chelons when applied in excess would also mask the zinc and suppress its polarographic wave completely. In the presence of large amounts of cadmium, with all chelons suitable for the purpose a wave of unknown origin occurred in the vicinity of the rising portion of the zinc wave. This interfering wave, although small, exhibits irregular behaviour and makes evaluation of the diffusion current of the zinc difficult. Thus, substoichiometric masking could not be successfully applied to solutions containing very large amounts of cadmium, but up to a cadmium to zinc ratio of about 50:1, the validity of the principle was confirmed. However, the application of substoichiometric masking to other systems has proved very successful. The results of these investigations will be published separately. Some quantitative considerations which allow a general evaluation of substoichiometric masking are presented below.

QUANTITATIVE CONSIDERATIONS

The theory will be restricted to 1:1 complexes (and hence essentially to reagents such as EDTA) because otherwise the orders of equations become so high that simplification requires approximations to be made that may not hold in practice. The expressions for the stability constants of the complexes formed by the reaction of the masking reagent, Y, with the metal to be determined, N, and the interfering metal, M, respectively, are

$$K_M = \frac{[MY]}{[M][Y]} \tag{1}$$

$$K_N = \frac{[NY]}{[M][Y]} \tag{2}$$

where K_M and K_N are the conditional stability constants for the complexes MY and NY, respectively. Charges are omitted for simplicity. The material balances for the system are

$$C_M = [M] + [MY] \tag{3}$$

$$C_N = [N] + [NY] \tag{4}$$

$$C_Y = [MY] + [NY] + [Y]. \tag{5}$$

Equations (1)–(5) will be used to derive an equation giving the relationship between the fraction of the metal N remaining uncomplexed when a fraction of the amount of masking reagent equivalent to the metal M present is added. In order to avoid an unpleasantly high-order equation the assumption will be made that the concentration of free masking reagent, Y, is sufficiently small to permit neglect of the term [Y] in equation (5). This assumption is reasonable because (*a*) the proposed masking procedure functions only if fairly stable complexes are involved, and because (*b*) there is always an excess of the metals present. Thus, equation (5) becomes

$$C_Y \sim [MY] + [NY]. \tag{6}$$

Obviously, the amount of N remaining uncomplexed will depend to a large extent on the ratio of the two stability constants which may be expressed as

$$Q = \frac{K_M}{K_N} = \frac{[MY]}{[M]}\frac{[N]}{[NY]} \tag{7}$$

Another factor having a significant influence on the fraction of metal N remaining uncomplexed is the amount of reagent Y added in relation to the amount of metal M present. This fraction, P, is given by

$$P = C_Y/C_M. \tag{8}$$

The term substoichiometric masking implies that $P < 1$.

Further, the ratio of the concentration of the metal N to that of the metal M will also have a significant influence. This ratio is expressed as

$$T = C_{\mathrm{M}}/C_{\mathrm{N}}. \tag{9}$$

A certain numerical value of T represents the relative interference threshold and may be denoted as $T_{i,r}$. T will always be a very small number because only the determination of small amounts of metal N in the presence of metal M is being considered.

The object of the treatment is to obtain an expression for the fraction of the metal N remaining uncomplexed when substoichiometric masking is applied. This fraction is given as

$$f = [\mathrm{N}]/C_{\mathrm{N}}. \tag{10}$$

An explicit expression for f as a function of the other parameters defined above is obtained as follows. A combination of equations (9) and (10) yields

$$[\mathrm{N}] = fC_{\mathrm{M}}/T. \tag{11}$$

A combination of equations (4), (9), and (11) yields

$$[\mathrm{NY}] = \frac{C_{\mathrm{M}}}{T} - \frac{fC_{\mathrm{M}}}{T} = \frac{C_{\mathrm{M}}}{T}(1 - f). \tag{12}$$

A combination of equations (6), (8), and (12) yields

$$[\mathrm{MY}] = PC_{\mathrm{M}} - \frac{C_{\mathrm{M}}}{T} + \frac{fC_{\mathrm{M}}}{T} = C_{\mathrm{M}}\left(P - \frac{(1 - f)}{T}\right). \tag{13}$$

A combination of equations (3) and (13) yields

$$[\mathrm{M}] = C_{\mathrm{M}}\left(1 - P + \frac{(1 - f)}{T}\right). \tag{14}$$

Substitution of the terms given by equations (11)–(14) into equation (7) yields

$$Q = \frac{P - \dfrac{(1 - f)}{T}}{1 - P + \dfrac{(1 - f)}{T}} \cdot \frac{f}{(1 - f)} \tag{15}$$

It is of considerable interest to note that the only term related to an absolute concentration (*i.e.*, C_{M}) cancelled out and that only the ratios of concentrations (and stability constants) are involved in this equation. Rearrangement of equation (14) yields the quadratic expression

$$f^2\frac{(Q - 1)}{T} - f\left[Q\left(1 - P - \frac{1}{T}\right) + \frac{(Q - 1)}{T} + P\right] + Q\left(1 - P + \frac{1}{T}\right) = 0. \tag{16}$$

Solving for f gives

$$f = \frac{A - \sqrt{A^2 - 4(Q - 1)\dfrac{Q}{T}\left(1 - P + \dfrac{1}{T}\right)}}{2(Q - 1)/T} \tag{17}$$

where $A = Q(1 - P + 1/T) + (Q - 1)T + P$. The root with negative sign should be used, as can be shown by evaluation of equation (7) at $P = 0$. This condition corresponds to the situation where no masking reagent has been added; then f must by necessity be unity. Equation (17) allows the calculation of the value of f for any given values of Q, P, and T. From such values conclusions may be made as to the degree of success to be expected from an application of substoichiometric masking under any set of conditions. However, a graphical representation permits a more rapid and direct insight into the situation. For this purpose, f is plotted as a function of P for a given value of T. One particular curve is obtained for each specified value of Q. A set of such curves for $T = 1{\cdot}0 \times 10^4$ is shown in Fig. 1. This value of T represents a case in which the metal N is to be determined at the 0·01 mole % level in the metal M. Only the range of greatest interest (*i.e.*, $1{\cdot}0 > P > 0{\cdot}8$) is shown.

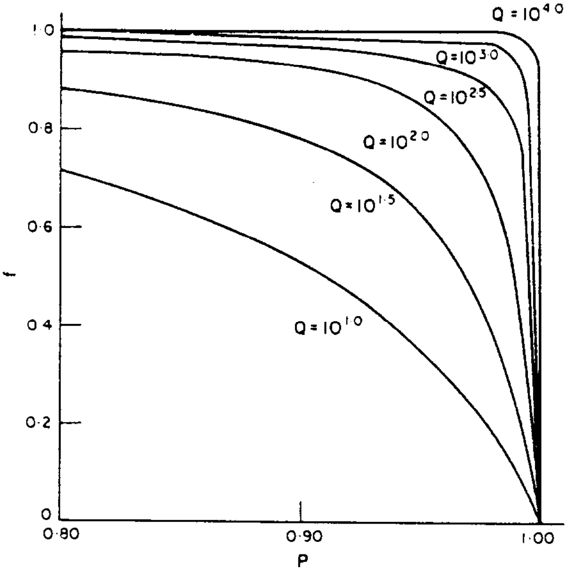

FIG. 1.—Fraction of uncomplexed metal N as a function of P for various values of Q, with T being $1{\cdot}0 \times 10^4$.

As was to be expected, the lower the value of Q, the less uncomplexed N is available. However, with $Q = 10^4$, the value for f is still 0·99 when P is 0·99. This indicates that 99% or essentially all of the metal to be determined is available when 99% of the interfering metal is complexed substoichiometrically. In this case, the original ratio of [free M]/C_N of 10000:1 has been reduced to only 100:1, which may be well below the interference threshold for some method of determination.

The derivation of equation (17) and the discussion thus far were based on the assumption that the determination of N is performed in such a manner that no shift in the equilibria is produced. This is the case, for example, when a polarographic finish is employed. However, if the procedure involves a reagent (*i.e.*, a complexing reagent), for example, for the purpose of a photometric finish, the situation becomes complex, but commonly also more advantageous. Suppose a chromogenic reagent is added to complex with the metal N. Usually this reagent will react preferentially with N and thus cause a favourable shift in the equilibrium. In more exact terms, the addition of an excess of this reagent with respect to N amounts to lowering the value of the conditional stability constant of the NY complex, and, thereby, increasing the value of Q. Even if both M and N react with the reagent, an advantage may be gained. If a separation step is involved (*i.e.*, and extraction or precipitation), only N and a very small amount of M will be separated from the bulk amount of M. The separated portion of the metals may then be subjected to some treatment which is satisfactory at the resulting low molar ratio.

A mathematical treatment of cases in which an additional reagent is present is possible, but with the larger number of equilibria to be considered (*i.e.*, those between N and possibly M and the added reagent), the resultant equation for f is third-order or higher. Such equations are difficult to handle and rarely allow a ready evaluation of the effects caused by changes in the various parameters. It is often possible to reduce the order of the equation by applying approximations. However, the familar situation then arises that the obvious or "clear cut" cases are well represented while the most interesting or "borderline" cases cannot be dealt with. Some of these cases have been treated mathematically, but the results are not presented here. In actual practice, a rough evaluation of the feasibility of substoichiometric masking can be made on the basis of the simple equation. This evaluation is used to design initial experiments and their results must then be used to gain insight as to how to proceed further.

The preceding derivation and discussion were made in terms of one metal to be determined in the presence of another. Substoichiometric masking, of course, is not restricted to such cases. It may be applied to other systems as well and in a fully analogous fashion.

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Zusammenfassung—Substöchiometrisches Maskieren liegt vor, wenn man ein Maskierungsmittel in einer Menge anwendet, die geringer als äquivalent der Menge zu maskierender Substanz ist. Hierbei wird die Menge an freier Störsubstanz unterhalb des störenden Niveaus (d.h. der "Störschwelle") gedrückt. Die Methode ist vorteilhaft in Fällen wo das Maskierungsmittel, wenn im Überschuss angewandt, die zu bestimmende Substanz nachteilig beeinflusst. Eine Formel zur Abschätzung substöchiometrischer Maskierung wird abgeleitet und eine generelle Diskussion der Möglichkeiten mitgeteilt.

Résumé—La dissimulation substoechiométrique est produite en ajoutant un agent dissimulant en quantité inférieure à celle équivalant à la substance à dissimuler. La quantité de substance gênante libre doit de ce fait être réduite à une valeur inférieure au seuil d'interférence, c'est-à-dire à la teneur à laquelle l'interférence intervient. La voie est avantageuse dans les cas où les agents dissimulants disponibles, lorsqu'ils sont ajoutes en excès, influent profondément sur la substance à doser. On établit des formules pour estimer les possibilités de réalisation de la dissimulation substoechiométrique et présente une discussion générale de la situation.

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SUBSTOICHIOMETRIC MASKING—II*

DETERMINATION OF TRACES OF COBALT IN NICKEL SALTS AND METALLIC NICKEL

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Summary—Cobalt is determined in the presence of large amounts of nickel by masking the latter substoichiometrically by addition of $\nless 98\%$ of the theoretically required amount of EDTA. The "free nickel":cobalt ratio is thereby decreased below the critical value and the cobalt is extracted as the green cobalt(III)–PAN complex into chloroform. Small amounts of nickel–PAN formed are destroyed by a subsequent EDTA–hydrochloric acid treatment. The absorbance of the treated extract is measured at 635 mμ. Copper, zinc, cadmium and iron do not interfere in ratios (to cobalt) of 500:1, 100:1, 100:1 and 10:1, respectively.

MANY cases exist in which the interference in the determination of one species due to another species becomes significant only when the ratio of the concentration of the species to be determined to that of the interferring species exceeds a certain relative interference threshold. Application of a masking reagent in the usual manner, *i.e.*, adding it in excess, is often impossible because the excess severely affects the reaction of the species to be determined. In such cases it may be feasible to add an amount of masking reagent less than that equivalent to the interfering species and thereby to bring the ratio of the concentration of the "free" interfering species to that of the species to be determined, below the interference threshold. A determination would then be possible. This approach is termed "substoichiometric masking" and some of its quantitative aspects have been discussed in Part I. Substoichiometric masking has been successfully applied to the determination of small amounts of cobalt in the presence of large amounts of nickel. The principles of this method and results of its application are described in the present paper.

In 1955 Cheng and Bray[1] introduced PAN (1-pyridylazo-2-naphthol) as a chromogenic reagent and compleximetric indicator. Among other metals, these authors also studied cobalt and found that on addition of PAN to a solution containing cobalt(II) and potassium periodate, a green cobalt(III)–PAN complex is formed which can be extracted into organic solvents. As was later shown by Flaschka and Raheem,[2] addition of an oxidant is not necessary in order to obtain this green complex, because seemingly the oxygen of the air dissolved in the solution is sufficient to effect the oxidation. This oxidation is accelerated by the presence of some water-miscible organic solvents, *e.g.*, ethanol. The green complex, once formed, is extremely stable and is not decomposed by strongly acidic medium even after remaining in it for hours or days. However, this complex does not form in strongly acidic solution. It seems that it is necessary to form first the weaker, red cobalt(II)–PAN complex which then is oxidized to the green cobalt(III)–PAN complex. Most other metals yield reddish PAN complexes, which are readily destroyed by addition of EDTA or acid [iron(III)

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* Part 1.—*Talanta*, 1958, **15**, 589.

is one exception]. Thus the formation of the green colour represents a quite selective reaction and at first glance may seem suitable for an unperturbed detection or photometric determination of cobalt in the presence of other metals. However, when these possibilities (especially the determination of small amounts of cobalt in nickel and its salts) were investigated, difficulties arose. If a small quantity of PAN is added to a solution containing cobalt and excessive amounts of nickel, most of the reagent is consumed by the nickel and only a small portion of the cobalt is transformed into the cobalt(II)–PAN complex. This amount of cobalt is oxidized to the green complex relatively rapidly. Then, however, the formation of more green complex becomes extremely slow, and on extraction low results for cobalt are obtained. Obviously, the release of PAN from its nickel complex is extremely slow even in a medium containing ethanol or other organic solvents which are added in order to avoid precipitation of PAN and its water-insoluble metal complexes. A complete and rapid formation of the green complex can be achieved only if PAN is added in an amount greater than that equivalent to the sum of cobalt and nickel. However, with large quantities of nickel present, such an amount is impracticable. Consequently, the determination of microgram amounts of cobalt in this manner is limited to a nickel:cobalt molar ratio of about 5:1. Since the rate of formation of the green cobalt(III)–PAN complex seems to be controlled by the rate at which PAN is released from its nickel complex the situation can be improved by using more PAN reagent and allowing longer reaction times. If a considerable excess (with respect to cobalt) of PAN is employed and the solution is allowed to stand for an hour or more with occasional vigorous shaking or, preferably, by passing a stream of air or oxygen through the solution, the complete formation of the green cobalt complex is achieved within an hour even in the presence of nickel at a Ni:Co molar ratio of 200:1. Although this ratio represents a considerable improvement, a relative interference threshold of 200 cannot be considered adequate since many methods exist which operate quite well at values far greater than this. However, this system seemed suitable for the application of "substoichiometric masking" with EDTA since the logarithmic stability constants of the EDTA complexes of cobalt and nickel (16·3 and 18·6 respectively) are only slightly over two logarithmic units apart. Calculations, made on the basis of the theoretical considerations presented in a Part I, indicated the feasibility of the approach even without taking into account the probably beneficial shift in equilibrium due to the addition of PAN ($T = 10^4$, $P = 0{\cdot}98$, $Q = 10^{2{\cdot}3}$ and from Fig. 1 of Part I, $f \sim 90\%$). However, because of the extent to which kinetic effects are involved, extreme caution was exercised when evaluating the results of these calculations, and experiments were made in order to reach a valid decision as to the feasibility of substoichiometric making. The evidence obtained from initial experiment was quite favourable, and, as will be shown below, a method was developed which allowed an adequately accurate, precise, and reasonably rapid extraction-photometric determination of small amounts of cobalt in the presence of large quantities of nickel.

EXPERIMENTAL

Reagents

Nickel solution $0{\cdot}5F$. Prepared by dissolving 29 g of nickel metal (99·9% pure) in a minimum amount of nitric acid (1 + 1) and diluting to 1 litre.

Cobalt solution, $0{\cdot}100F$. Prepared by dissolving 1·473 g of cobalt metal (99·9% pure) in a minimum amount of nitric acid (1 + 1) and diluting to 250 ml. A $2{\cdot}00 \times 10^{-4}F$ cobalt solution was prepared by an appropriate dilution of this stock solution.

EDTA solution, 0·1*F*. Prepared by dissolving 37 g of the disodium salt in water and diluting to 1 litre.

PAN solution, 0·010*F*. Prepared by dissolving 0·622 g of reagent grade material in 95% ethanol and diluting to 1 litre.

Procedure

Dissolve the sample and dilute with water to known volume (Note 1). Take one or two small aliquots and titrate with the 0·1*F* EDTA solution (Note 2). Take an aliquot of the sample solution corresponding to 20–300 μg of cobalt and add 0·1*F* EDTA solution in an amount sufficient to decrease the molar ratio of "free Ni":Co below a value of 200:1 (Note 3). Add 96% ethanol until the resulting solution contains 50–60% v/v alcohol. Add to the solution hydrochloric acid (1 + 1) or dilute ammonia until pH is 2·0–2·5 (measured by pH meter). Transfer the solution to a separating funnel, add 5 or 10 ml of PAN solution and aerate for at least one hour with air or oxygen (Note 4). After the green colour has developed, add enough water to bring the ethanol concentration below 20% v/v. Add 2–3 ml of 0·1*F* EDTA to the resultant solution, shake it and allow it to stand for 1–2 min. Extract with 10-ml portions of chloroform until the extract is colourless. To the combined extracts add enough concentrated hydrochloric acid to give a final concentration of 2 ml of this acid per 100 ml of final solution. Dilute to volume with 96% ethanol and measure the absorbance of the solution at 625 mμ against a reference solution containing identical concentrations of hydrochloric acid and PAN. Evaluate by means of a calibration curve prepared by carrying through the procedure a series of 50% v/v ethanol–water mixtures containing increments between 1 and 25 ml of $2 \times 10^{-4}F$ cobalt solution.

Notes. (1) Nickel metal is dissolved in the minimum amount of nitric acid (1 + 1) with warming. Nickel salts may be dissolved in water containing a few drops of an acid.

(2) The titration is performed conventionally in an ammoniacal solution with Murexide as indicator or at pH 4–5 in the presence of some copper–EDTA at an elevated temperature with PAN as indicator.[3]

(3) If the amount of cobalt and thus the Ni:Co ratio are completely unknown a rough predetermination may be performed by carrying an aliquot of the sample solution through the procedure outlined above, after adding 98% of the amount of EDTA equivalent to the metals in the sample. The solution is then aerated for about an hour in the oxidation step. The conditions for the subsequent actual determination should be designed according to the result obtained in this rough determination.

(4) Alternatively the solution may be shaken vigorously at short intervals. For the application of longer aeration times see *Discussion and Results*.

(5) Since no nickel is present in the standards, addition of EDTA can be omitted and the 1-hr aeration period is shortened to 5 min of vigorous shaking before extraction.

RESULTS AND DISCUSSION

The results of several photometric determinations of cobalt, alone and in the presence of nickel are presented in Table I. For solutions containing Ni:Co molar ratios in excess of 2000:1 a small correction for the trace amounts of cobalt introduced with the nickel stock solution was necessary. A determination of the amount of cobalt in this nickel solution according to the procedure outlined gave an insignificantly higher value than that obtained in a polarographic determination.* The use of either result for the correction of experimental values produced essentially the same correction factor. The observed slight tendency towards negative errors is probably due to the incomplete formation of the cobalt(III)–PAN complex.

The optimum pH range for the formation of the green cobalt complex was found to be pH 2·0–2·5. At a pH higher than 2·5, a lower rate of formation was observed, and at a pH lower than 2·0, erratic results were obtained.

A 50% v/v ethanol–water solution is necessary in order to prevent the precipitation of water-insoluble metal–PAN complexes. Incomplete colour development was observed in solutions which became turbid owing to the precipitation of these complexes (predominantly the nickel–PAN complex). In cases where a considerable amount of

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* Performed by Mr. Wm. Wolfram, J. T. Baker Chemical Co., Phillipsburg, N.J., whose aid is greatly appreciated.

TABLE I.—REPRESENTATIVE RESULTS OF THE PHOTOMETRIC DETERMINATION OF COBALT IN NICKEL

Cobalt, $2{\cdot}0 \times 10^{-4}F$			Ni:Co, Molar ratio
Added, *ml*	Found, *ml*	Difference, *ml*	
10·00	10·00	0·00	100*
10·00	10·00	0·00	100*
10·00	9·90	−0·10	200†*
10·00	9·95	−0·50	200†*
10·00	10·00	0·00	500
8·00	7·97	−0·03	700
10·00	10·00	0·00	1000
5·00	5·00	0·00	1000
8·00	8·01	+0·01	1000
15·00	14·95	−0·05	1000
5·00	4·97	−0·03	2000
10·00	10·05	+0·05	2000
8·00	8·00	0·00	2500
8·00	7·95	−0·05	3000
10·00	10·00	0·00	3000
5·00	5·00	0·00	6000
10·00	10·00	0·00	6000
15·00	14·95	−0·05	6000
5·00	5·00	0·00	8000
10·00	9·95	−0·05	8000
10·00	10·00	0·00	10000
8·00	8·00	0·00	12000
10·00	9·95	−0·05	15000†
5·00	4·97	−0·03	20000†
10·00	9·95	−0·05	20000†
10·00	9·97	−0·03	20000†

* No EDTA added.
† Aerated for 2 hr.,

"free" nickel was present, 60–70% v/v ethanol-water solutions were often necessary. On the addition of chloroform to solutions containing such a high proportion of ethanol, only a single phase is formed. Thus, in order to ensure the formation of two phases and their adequate separation, a considerable quantity of water must be added before the extraction can be carried out.

The nickel-PAN complex, if extracted along with the cobalt(III)-PAN complex, interferes with the photometric determination since it absorbs slightly at 624 mμ. In order to avoid this interference, the PAN-complexes of nickel and other metals are destroyed by the addition of excess of EDTA before extraction. Further, hydrochloric acid is added to the extract to decompose any traces of metal complexes (other than those of cobalt) which may have survived the EDTA treatment.

The rule that the "free Ni": Co molar ratio should be 200: 1 or less cannot be strictly followed for solutions containing extremely large amounts of nickel. For such solutions, reduction of the original ratio to a value of 200: 1 necessitates the addition of over 99% of the stoichiometric amount of EDTA. In such cases slightly negative errors in the pretitrations may lead to the addition of an excess of EDTA and result in the complexation of some or even all of the cobalt. Therefore, for solutions having Ni: Co molar ratios in excess of 5000: 1, it is more practical to add 98% of the volume of EDTA required. The resultant solutions have "free Ni": Co molar ratios higher than the prescribed 200:1. The addition of a larger amount of PAN solution (15 ml) or aeration for a longer period of time, or both, is then necessary to develop the green colour fully. With this modification applied, two hours' aeration was found to be sufficient for Ni:Co ratios up to 20000:1. It should be pointed out that further investigations are being conducted to study the mechanism of the oxidation of the cobalt(II)–PAN to the cobalt(III)–PAN complex. It is not fully clear whether the oxidation is caused by dissolved oxygen or by other species present in the solution. The only experimental fact at hand is that passing a stream of air or oxygen leads faster to full development of the green colour than does mere standing with occasional shaking.

It is quite possible that substoichiometric masking in combination with a chloroform extraction of the green cobalt(III)–PAN complex may be applied to the determination of cobalt traces in other metals or salts. In the present study, however, the influence of other metals was investigated with these metals at ratios which might be expected as additional low-level impurities. Calcium, magnesium and aluminium have no influence. Copper(II) forms a quite stable EDTA complex and when substoichiometric masking is applied to eliminate the influence of the nickel, copper is almost completely complexed by EDTA. Small quantities of copper combining with PAN are eliminated by the addition of excess of EDTA after the development of the green colour or by addition of hydrochloric acid to the combined extracts. Copper was tested in amounts up to a Cu:Co molar ratio of 500:1 and found to have no influence on the cobalt determination.

Cadmium and zinc had no influence at molar ratios up to 100:1. However, the rate of formation of the Co(III)–PAN complex seemed to be decreased slightly at Cd:Co or Zn:Co molar ratios greater than about 10:1, and a longer aeration period (about 2 hr) was found to be necessary.

Iron(III) forms an extractable red PAN complex which is destroyed neither by the addition of excess of EDTA nor by the addition of hydrochloric acid to the combined extracts. Thus, iron(III) not only decreases the concentration of "free" PAN in the solution, thus reducing the amount of reagent available for the formation of the cobalt(II)–PAN complex, but also interferes with the photometric determination, owing to the absorbance of the iron(III)–PAN complex at 625 mμ. Unexpectedly, this complex is formed even when substoichiometric masking of nickel with EDTA is applied. Iron(III) can only be tolerated at Fe:Co molar ratios up to 10:1.

Acknowledgement—The work was aided in part by a grant from the National Science Foundation, Washington, D.C. This help is greatly appreciated.

Zusammenfassung—Kobalt kann in Gegenwart von hohen Nickelmengen bestimmt werden, wenn letzteres Metall durch substöchiometrische Maskierung mittels Zusatz von $\nless$98 Prozent der theoretisch benötigen Menge an ÄDTE ausgeschaltet wird. Hierbei wird das Verhältnis "freies Nickel":Kobalt unter die Störschwelle gedrückt und das Kobalt kann komplett als grüner Kobalt(III)-PAN Komplex mit Chloroform extrahiert werden. Kleine Mengen an mitextrahiertem Nickel-PAN Komplex werden durch eine nachträgliche Behandlung mit ÄDTE und Salzsäure unschädlich gemacht. Die Extinktion des behandelten Extraktes wird bei 625 mμ gemessen. Kupfer, Zink, Kadmium und Eisen stören nicht in Verhältnissen (zu Kobalt) von 500:1, 100:1, 100:1, bzw. 10:1.

Résumé—On dose le cobalt en la présence de grandes quantités de nickel en dissimulant ce dernier substoechiométriquement par addition d'environ 98% de la quantité théoriquement requise d'EDTA. Le rapport "nickel libre":cobalt est ainsi abaissé en dessous de la valeur critique et l'on extrait le cobalt en chloroforme à l'état de complexe vert cobalt (III)-PAN. De petites quantités de nickel-PAN formé sont détruites par un traitement subséquent EDTA-acide chlorhydrique. L'absorption de l'extrait traité est mesurée à 625 mμ. Le cuivre, le zinc, le cadmium et le fer n'interfèrent pas dans des proportions (par rapport au cobalt) de 500:1, 100:1, 100:1 et 10:1 respectivement.

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ARSENAZO III AND ITS ANALOGUES—V

COMPLEX FORMATION OF NIOBIUM WITH *o,o'*-DIHYDROXYAZO COMPOUNDS

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Summary—A new group of reagents—the 2,7-bisazo derivatives of chromotropic acid—has been synthesized and the reaction of these compounds with niobium studied. Reaction with niobium occurs in strongly acidic medium (1–3*N*) and is characterized by high sensitivity ($\varepsilon = 30$–50×10^3). The functional grouping responsible for the reaction was shown to be the *o,o'*-dihydroxyazo group. The analytical usefulness of the reagents is determined by the presence of the electron-withdrawing substituents and the nature of the diazo coupling component. Niobium reacts in partially hydrolysed form with these reagents, to give 1:1 complexes.

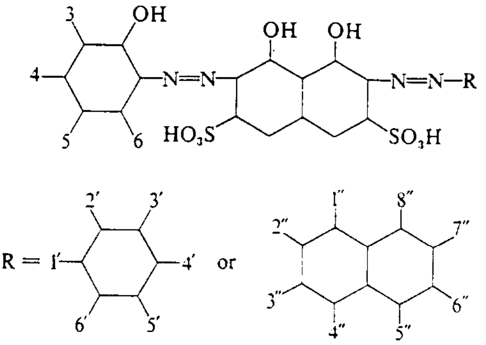
IN PREVIOUS works[1,2] some 2,7-bisazo derivatives of chromotropic acid, containing an *o,o'*-dihydroxyazo grouping, were examined as reagents for the photometric determination of niobium, and seemed promising reagents for some other metals.[3,4] One of these reagents—sulphochlorophenol C—has come to be widely used for the determination of niobium.[5] Further study of this class of compound has led to the finding of a series of more sensitive and useful reagents, enumerated in Table I together with details of their reaction with niobium. Figure 1 shows the absorption spectra of reagent and complex, and Fig. 2 shows the effect of acidity on the colour development. The reagents give similar colour reactions with a series of other elements—zirconium, hafnium, vanadium, molybdenum, copper, scandium, aluminium, indium, gallium and palladium—and can be used for their determination. The present work deals with the niobium reaction.

THE FUNCTIONAL GROUP

It has been reliably established that in the monoazo compounds such as Lumogallion or Anthracene Chrome Violet, the *o,o'*-dihydroxyazo group is functional for niobium, but for the group of reagents studied here (the azo derivatives of chromotropic acid) more exact definition is required. The peri-dihydroxy group of the chromotropic acid may also be active. According to Ackermann and Koch[6] this grouping is characteristic for niobium, and niobium has been determined with chromotropic acid.[7]

Our results show, however, that the presence of these groupings is not itself sufficient for a colour reaction to occur with niobium. The structure of the whole molecule must be taken into account, and the modern approach to consideration of functional groups considers not only specific elements of the structure of a given

TABLE I.—COLOUR REACTION OF NIOBIUM WITH 2,7-BISAZO DERIVATIVES OF CHROMOTROPIC ACID



No.	Substituents	Name of reagent	Reaction conditions, [HCl], M	$\Delta\lambda$, $m\mu$	ε
1	5-nitro-3,3′-disulphonic acid	sulphonitrophenol M	3	80	53000
2	5-nitro-3,4″,8″-trisulphonic acid		0·1	90	50000
3	5-chloro-2′-carboxylic-3-sulphonic acid	sulphochlorophenol K	1·5	80	50000
4	5-chloro-3,3″,8″-trisulphonic acid	sulphochlorophenol AE	2	60	48600
5	5-nitro-3,3″,8″-trisulphonic acid	sulphonitrophenol AE	1	80	48000
6	5-chloro-3-sulphonic acid	sulphochlorophenol B	2	90	44000
7	5-chloro-3,3′-disulphonic acid	sulphochlorophenol M	2·5	90	43000
8	3,5-dinitro-3′-sulphonic acid	picramine M	2·5	60	42000
9	3,5,5′-trinitro-2-hydroxy-3′-sulphonic acid		3	50	42000
10	2-carboxylic-5-nitro-3-3-sulphonic acid	sulphonitrophenol K	3	95	40000
11	3,5-dinitro-2-carboxylic acid	picramine K	1	95	40000
12	3,5-dinitro-3″,8″-disulphonic acid	picramine AE	1	80	38000
13	5,5′-dichloro-2′-hydroxy-3-sulphonic acid		1	60	36000
14	5,5′-dinitro-2′-hydroxy-3,3′-disulphonic acid	sulphonitrophenol S	2	85	33000
15	5,5′-dichloro-2′-hydroxy-3,3′-disulphonic-acid	sulphochlorophenol S	1·5	80	33000
16	5-chloro-2′-hydroxy-3,5′-disulphonic acid		2	80	31500
17	3,3′,5,5′-tetranitro	picramine S	6	50	30000

S = symmetrical; K = carboxyl; B = benzene; M = metanilic acid; AE = amino-ε-acid. The nature of the diazo coupling component or the substituent in it that is *ortho* to the azo grouping is indicated. In reference 2, S was incorrectly transliterated as C in sulphonitrophenol S etc.

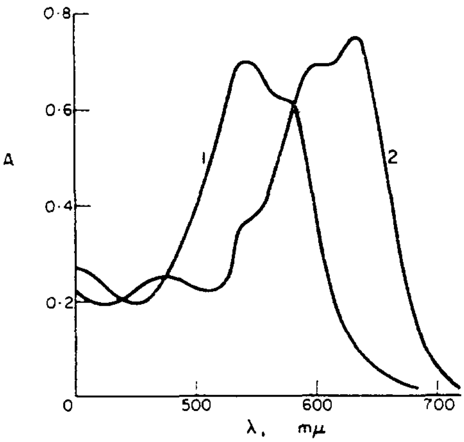


FIG. 1.—Absorption spectra of sulphonitrophenol M (*1*) and its niobium complex (2).

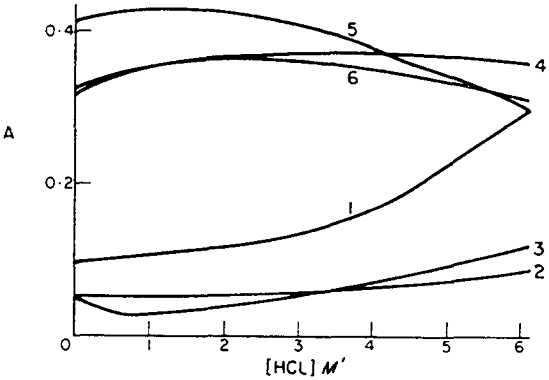
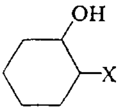
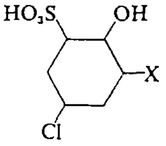


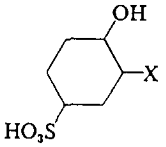
FIG. 2.—Effect of acidity on the maximum absorbance at 640 mμ of various reagents and their niobium complexes.
1—Sulphochlorophenol K, 0·8 × $10^{-5}M$: *2*—sulphonitrophenol C, 1·08 × $10^{-5}M$: *3*—sulphonitrophenol M, 1·46 × $10^{-5}M$: *4*—Nb complex of *1*; *5*—Nb complex of *2*: *6*—Nb complex of *3*.

compound but also those or related compounds, and we therefore synthesized several compounds of the type under investigation.

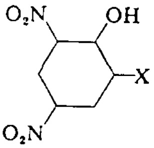
In general, monoazo compounds of chromotropic acid gave either no colour reaction with niobium or a reaction of such little colour contrast that it was not analytically useful. In the first group were the compounds

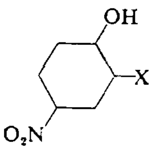


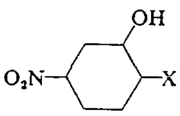




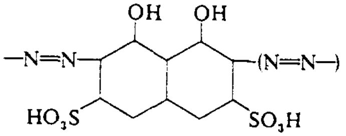
and in the second



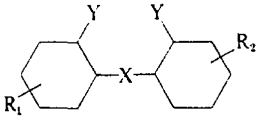




where (and subsequently) X denotes

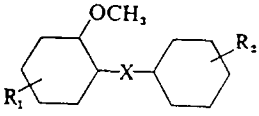


Thus in the case of the azo derivatives of chromotropic acid, the second diazo component determines the analytical usefulness of the reagent. Study of a series of bisazo compounds which did not contain hydroxy groups in the benzene rings showed that compounds of this type do not give interesting colour reactions with niobium:

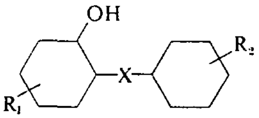


where Y = $-AsO_3H_2$, $-COOH$, $-SO_3H$.

A negative result was also obtained with compounds based on *o*-anisidine:



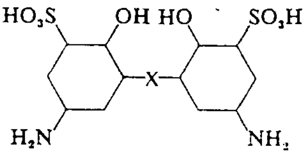
whereas reagents derived from *o*-aminophenol gave a distinct colour reaction with niobium:



We therefore conclude that the *o*,*o*′-dihydroxyazo grouping is the functional group of niobium complexation by the 2,7-bisazo derivatives of chromotropic acid.

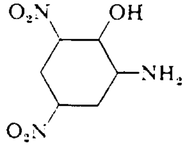
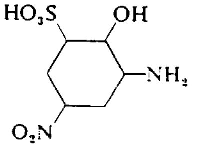
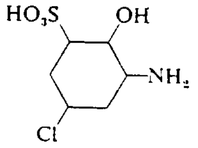
INFLUENCE OF SUBSTITUENTS

From Table I, which shows the best reagents for niobium, it can be seen that almost all of these contain two electron-withdrawing substituents. The presence of only one such group is insufficient to make the reagent analytically useful, and introduction of a donor group severely impairs the complex-forming properties of the reagent. Thus reduction of sulphonitrophenol S with sodium sulphide in acetic acid medium gives a compound with practically no colour reaction with niobium. The same thing happens with reduction of picramine S or M, *etc.*

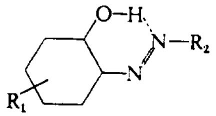


The nature and position of the electron-withdrawing substituents is important.

The most interesting reagents were obtained by using the following aromatic amines.

Other well-known reagents such as Lumogallion also contain electron-withdrawing substituents *ortho* and *para* to the hydroxy group. Evidently the influence of these substituents is connected with their effect on the ionization of the hydroxy group. Furthermore, in the absence of such substituents we may expect internal hydrogen bonding

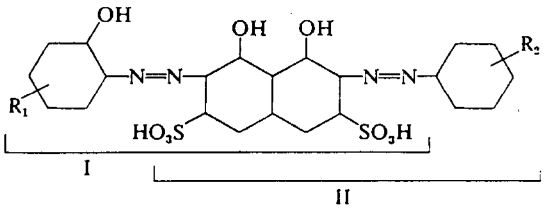


with consequent deactivation of the reagent in complex-formation.[8] It is also important that these substituents appear to act as auxochromes, leading to a better colour contrast in the reaction.

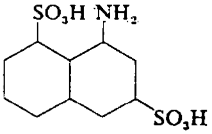
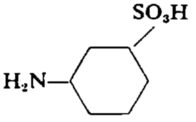
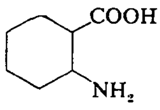
INFLUENCE OF THE SECOND COUPLING COMPONENT

From the niobium complexes of a series of compounds synthesized from the same coupling compounds (*e.g.*, 2-amino-5-chloro-3-hydroxybenzenesulphonic acid and 2-amino-3-hydroxy-5-nitrobenzenesulphonic acid) it is evident that the colour reaction depends on the nature of the second coupling component even though this plays no direct part in the metal bonding.

The electronic structure of the 2,7-bisazo derivatives of chromotropic acid shows that these contain essentially two partially conjugated systems each of which includes the azo group, the naphthalene nucleus, and the substituted benzene nucleus:[9]

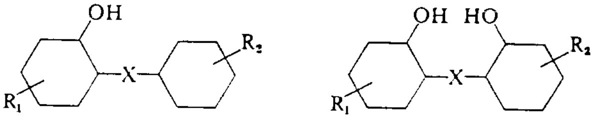


As a result of the partial conjugation, the second coupling component influences the reactivity of the functional grouping and the absorption spectrum of the metal complex. Its effect is also determined by its spatial location, its electron-withdrawing properties, the possibility of internal hydrogen-bonding, and the possibility of tautomerism. Table I shows that the best reagents are those with a symmetrical structure or containing an anthranilic, metanilic, or ε-amino acid as second coupling component:

COMPOSITION AND STRUCTURE OF THE COMPLEXES

The reagents synthesized contain either one or two *o,o'*-dihydroxyazo groups:

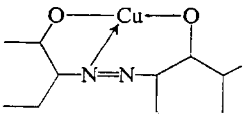


the second of these does not appear to influence the analytical properties of the reagent, so it may be concluded that only one of the groups is reactive. This conclusion is reached from a study of the composition of the complexes (obtained by the usual methods—the details are not given here), which are all 1:1 except for the picramine S complex which has a metal:reagent ratio of 1:2. This exception is in agreement with Pfitzner's principle,[10] which states that reagents containing smaller numbers of salt-forming groups (whether participating in complex formation or not) form complexes containing a higher proportion of reagent.

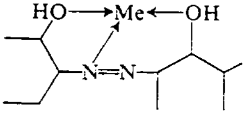
In the general case the stoichiometry of the reaction does not indicate whether the complex is monomeric or polymerized, but the study of a series of reagents of similar structure permits conclusions to be drawn on this point. When 1:1 complexes are formed with reagents which have an asymmetric structure, only one structure is possible for the niobium complex (unless there are intermolecular associations, but we did not consider this possibility). With symmetrical reagents, however, it is *a priori* impossible to differentiate between 1:1 and 2:2 complexes from the stoichiometry. There are, however, no reasons for supposing that symmetric reagents react by a different mechanism from that for asymmetric reagents, so it is more likely that the complexes are all monomeric, in agreement with the findings for the arsenazo III complexes of thorium, uranium and lanthanum.[9] The mechanism is connected with the fact that in formation of the complex with one of the functional groupings, a positive charge is induced on the azo group of the second functional grouping, and this hinders formation of the second nitrogen-metal bond. Only with certain typical transition metals (copper, vanadium and molybdenum) are complexes found with a 2:1 metal:reagent ratio, and this can be explained by π-back-bonding with its attendant equalization of the charge and stabilization of the metal bonding with both azo groups.

In some cases the complex precipitates on long standing. It seems that this does not indicate a change in the structure of the complex or polymerization, but rather the agglomeration of micro-particles of a low-solubility complex. The stoichiometry remains the same.

Establishment of the structure of the complex is more complicated. For cations such as copper(II) which react in weakly acidic solution, it was possible to determine by potentiometry the number of protons released, and on this basis to propose the structure



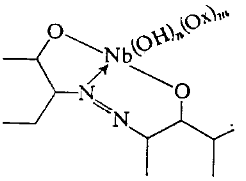
Such direct methods are not possible for complexes formed in strongly acidic solution, and the indirect methods are not very reliable. There is no convincing proof that the reaction mechanism is the same in weakly and strongly acidic media, and in the latter, where ionization of the hydroxy group is suppressed, the structure

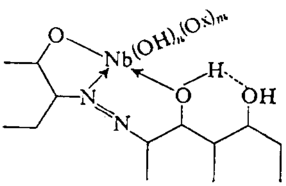


cannot be excluded from examination. Certainly for the zirconium-arsenazo III system the spectrophotometric data indicate that the mechanism changes with the acidity, protons being released in weakly acidic but not in strongly acidic media.[4]

Experiments with the reagents containing a substituted hydroxy group (the anisidine reagents mentioned earlier) gave some indirect information. The presence of a liable hydrogen atom in the hydroxy group on the benzene ring appears to be an essential condition for the reactivity of the *o*,*o*′-dihydroxyazo grouping for niobium, though it should be noted that the anisidine-type reagents will react with copper(II).

The second problem is the nature of the reactive niobium species. Much has been written on this, but the problem is far from being solved. We accept the findings[11,12] that in 1–3*M* hydrochloric acid niobium exists as a partially hydrolysed species and that its complexes can form mixed ligand complexes with the anions of mineral acids or oxy-acids (Ox, *e.g.*, tartrate and citrate). We can therefore postulate the following structures for the niobium complexes of those *o*,*o*′-dihydroxy compounds:





Zusammenfassung—Eine neue Gruppe von Reagentien—die 2,7-Bisazoderivate der Chromotropsäure—wurde dargestellt und die Reaktion dieser Verbindungen mit Niob untersucht. Die Reaktion mit Niob findet in stark saurem (1–3 N) Medium statt und ist durch hohe Empfindlichkeit gekennzeichnet ($\varepsilon = 30\text{–}50 \cdot 10^3$). Es wurde gezeigt, daß die für die Reaktion verantwortliche Gruppierung die *o*,*o*′-Dihydroxyazogruppe ist. Der analytische Nutzen der Reagentien wird durch die Gegenwart der elektronensaugenden Substituenten und die Natur der Diazokupplungskomponente bestimmt. Niob reagiert in teilweise hydrolysierter Form mit den Reagentien zu 1:1-Komplexen.

Résumé—On a synthétisé un nouveau groupe de réactifs, les dérivés 2,7-bisazo de l'acide chromotropique, et étudié la réaction de ces composés avec le niobium. La réaction avec le niobium a lieu en milieu fortement acide (1 — 3*N*) et est caractérisée par une sensibilité élevée ($\varepsilon = 30 - 50 \times 10^3$). On a montré que le groupement fonctionnel responsable de la réaction est le groupe *o*,*o*′-dihydroxyazo. L'intérêt analytique des réactifs est déterminé par la présence des substituants attracteurs d'électrons et la nature du composant de diazocopulation. Le niobium réagit sous forme partiellement hydrolysée avec ces réactifs, donnant des complexes 1:1.

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STUDIES ON URANYL COMPLEXES—III

URANYL COMPLEXES OF EDTA*

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Summary—The uranyl complexes of EDTA have been studied by potentiometry; stability constants of the 1:1 and 2:1 (metal to ligand) chelates have been determined, as well as the respective hydrolysis and polymerization constants. Possible structures for these species are discussed. To account for the abnormally high stability of $UO_2(H_2O)HL^-$, hydrogen bonding between a protonated nitrogen atom of the ligand and one oxygen atom of UO_2^{2+} is suggested.

THE STUDY of the complexes formed by the uranyl cation with the polyaminocarboxylic acids may be of considerable interest for the understanding of the behaviour of this ion in aqueous solution. The species formed are generally quite stable, and the mathematical treatment of the corresponding equilibria is not too involved.

In the first paper of this series[1] we presented stability constants for the complexes formed by the uranyl ion with ethyleneglycol-bis(aminoethyl-ether)tetra-acetic acid (EGTA); 1:1 and 2:1 species were identified, but since we were only interested in possible direct analytical applications, polynuclear olated species were not considered.

We have also reported values for the stability constants of the so-called "normal" complexes of 12 iminodiacetate derivatives and have shown that these could be represented by the linear equation

$$\log K_{ML} = 1{\cdot}19 \log K_{HL} - 1{\cdot}87$$

with a mean deviation of $\pm 0{\cdot}25$ in the estimated values of $\log K_{ML}$, at the 95% level of significance.[2] The 1:1 complex of UO_2^{2+} with EDTA behaved abnormally, prompting the closer study of this system which is now reported.

EXPERIMENTAL

Reagents

Ethylenediaminetetra-acetic acid (EDTA). Very pure ethylenediaminetetra-acetic acid was obtained by acidifying to about pH 2 a solution of Fisher "certified" disodium salt of EDTA, and recrystallizing the product from demineralized water.

Uranyl nitrate. A Merck analytical grade product was used; solutions were standardized gravimetrically by ignition of precipitated ammonium diuranate to triuranium octaoxide.

Carbonate-free potassium hydroxide solutions. Carbonate-free potassium hydroxide, concentration $C_B = 0{\cdot}100M$ and $1{\cdot}00M$, was prepared according to the instructions of Schwarzenbach and Biedermann.[3] The ionic strength was adjusted by addition of potassium nitrate, to compensate for neutralization of hydroxide ions during the titrations.

Instruments

pH measurements and titrations were made with a Radiometer PHM 4 instrument, with a Radiometer type G 2025 B glass electrode and a saturated calomel electrode as reference.

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Technique

Details of the experimental procedures have been given elsewhere;[4] measurements were conducted in media of ionic strength 1·00*M* (and also 0·100*M* for the simple species) maintained with potassium nitrate; the temperature was controlled to 25·0 ± 0·1° by circulating water through double-walled titration and reference cells. The total concentration of both the uranyl ion and EDTA varied between 5·0 × $10^{-4}M$ and 5·0 × $10^{-3}M$ (five different concentrations for the 1:1 species and four different concentrations for the 2:1 species, as indicated in Figs. 3 and 4).

Experimental results are presented only in the form of titration or n_H *vs.* pH curves, but data will be made available on request.

CALCULATIONS

The following conventions will be adopted: the protonated species of the ligand will be denoted by H_iL, the uranyl ion by M, the $UO_2(H_2O)HL$ chelate by MHL or $MHL.H_2O$, the $(UO_2)_2(H_2O)_2L$ chelate by M_2L or $M_2L.H_2O$, *etc.*

The corresponding formation constants will be represented by K_i^H, K_{MHL}, K_{M_2L}, etc. Ionization constants will be denoted by *k*'s and overall formation constants by *β*'s.

Co-ordinated water molecules and charges will be omitted for the sake of simplicity, except when necessary for better understanding of the argument or derivations.

The stability constant of the complex $UO_2(H_2O)HL^-$: MHL

The mass balances for the ligand and for the metal are the following:

$$C_L = [H_4L] + [H_3L] + [H_2L] + [HL] + [MHL] \qquad (1)$$

$$C_M = [M] + [MHL] \qquad (2)$$

On the other hand, the electroneutrality condition demands

$$[K^+] + [H^+] + 2[M^{2+}] = [H_3L^-] + 2[H_2L^{2-}] + 3[HL^{3-}] + [MHL^-] + [NO_3^-] + [OH^-] \qquad (3)$$

where $[K^+]$ is the concentration of potassium ion introduced during the titration and $[NO_3^-] = 2C_M$ is the concentration of nitrate ion added as uranyl nitrate.

From equations (1), (2) and (3) may be derived

$$(3 - a)C_L - [H] + [OH] = 3[H_4L] + 2[H_3L] + [H_2L] \qquad (4)$$

and

$$[M] = C_M - C_L + \alpha_H[HL] \qquad (5)$$

In these equations *a* is the "degree of neutralization", defined as the number of equivalents of base added per mole of ligand. Hence, from equation (4):

$$[HL] = \frac{(3 - a)C_L - [H] + [OH]}{\beta_H}. \qquad (6)$$

The terms α_H and β_H are given by

$$\alpha_H = 1 + \sum_{i=1}^{3} \beta_i^H[H^+]^i$$

$$\beta_H = \sum_{i=1}^{3} i\beta_i^H[H^+]^i \qquad (7)$$

where the $\beta_i{}^{\mathrm{H}}$ are the overall formation constants of the species $\mathrm{H}_i\mathrm{L}$.

The stability constant of the complex $\mathrm{UO_2(H_2O)HL^-}$ is calculated from

$$K_{\mathrm{MHL}} = \frac{C_{\mathrm{M}} - [\mathrm{M}]}{[\mathrm{M}][\mathrm{HL}]}, \tag{8}$$

[M] and [HL] being given by equations (5) and (6).

The stability constant of the complex $\mathrm{(UO_2)_2(H_2O)_2L : M_2L}$

The mass balances to be considered are the following:

$$C_{\mathrm{L}} = [\mathrm{H_4L}] + [\mathrm{H_3L}] + [\mathrm{H_2L}] + [\mathrm{HL}] + [\mathrm{L}] + [\mathrm{MHL}] + [\mathrm{M_2L}] \tag{9}$$

$$C_{\mathrm{M}} = [\mathrm{M}] + [\mathrm{MHL}] + 2[\mathrm{M_2L}] \tag{10}$$

The electroneutrality condition takes the form:

$$[\mathrm{K^+}] + [\mathrm{H^+}] + 2[\mathrm{M^{2+}}] = [\mathrm{H_3L^-}] + 2[\mathrm{H_2L^{2-}}] + 3[\mathrm{HL^{3-}}] + 4[\mathrm{L^{4-}}] + [\mathrm{MHL^-}] + [\mathrm{NO_3^-}] + [\mathrm{OH^-}] \tag{11}$$

From equations (9), (10) and (11) may be derived

$$[\mathrm{L}] = \frac{(4 - a)C_{\mathrm{L}} - [\mathrm{H}] + [\mathrm{OH}]}{\beta_{\mathrm{H}} + K_{\mathrm{MHL}} \cdot \beta_1{}^{\mathrm{H}} \cdot [\mathrm{H}][\mathrm{M}]} \tag{12}$$

and

$$C_{\mathrm{M}} - 2C_{\mathrm{L}} = [\mathrm{M}] - 2\alpha_{\mathrm{H}}[\mathrm{L}] - [\mathrm{MHL}] \tag{13}$$

Hence

$$[\mathrm{M}] = \frac{C_{\mathrm{M}} - 2C_{\mathrm{L}} + 2\alpha_{\mathrm{H}}[\mathrm{L}]}{1 + K_{\mathrm{MHL}} \cdot \beta_1{}^{\mathrm{H}}[\mathrm{H}][\mathrm{L}]} \tag{14}$$

Here α_{H} and β_{H} are again given by equations (7), with the sums extended to $i = 4$.

Equations (12) and (14) can be solved simultaneously by an iterative procedure and $\beta_{\mathrm{M_2L}}$ is calculated from the definition:

$$\beta_{\mathrm{M_2L}} = \frac{[\mathrm{M_2L}]}{[\mathrm{M}]^2[\mathrm{L}]} = \frac{C_{\mathrm{M}}\text{-}[\mathrm{M}] - K_{\mathrm{MHL}} \cdot \beta_1{}^{\mathrm{H}}[\mathrm{H}][\mathrm{M}][\mathrm{L}]}{2[\mathrm{M}]^2\,[\mathrm{L}]}$$

$$= \frac{C_{\mathrm{M}} - [\mathrm{M}]\{1 + K_{\mathrm{MHL}} \cdot \beta_1{}^{\mathrm{H}}[\mathrm{H}][\mathrm{L}]\}}{2[\mathrm{M}]^2 \,.\, [\mathrm{L}]} \tag{15}$$

Stability constants and formulae of the polynuclear olated species

The formulae and formation constants for the polynuclear species formed by olation of the 1:1 complexes were calculated by Sillén's method of comparing experimental data with normalized curves.[5,6]

For the species formed by olation of the 2:1 complexes, Sillén's "core + links" method[7,8] was used as described below. The symbols adopted in this section are those used by Sillén.[5,8]

RESULTS AND DISCUSSION

Simple species

Titration curves of 1:1 and 2:1 mixtures of EDTA and uranyl nitrate are presented in Fig. 1.

The inflexion at $v \sim 3$ ml in curve (2) suggests that a protonated UO_2HL^- complex is formed, but two more protons are titrated up to $v \sim 5$ ml, and it is legitimate to assume that there exists a co-ordinated water molecule which ionizes to form the hydroxo-complex $UO_2(OH)HL^{2-}$ and the probable dimeric species $(UO_2)_2(OH)_2H_2L_2{}^{4-}$.

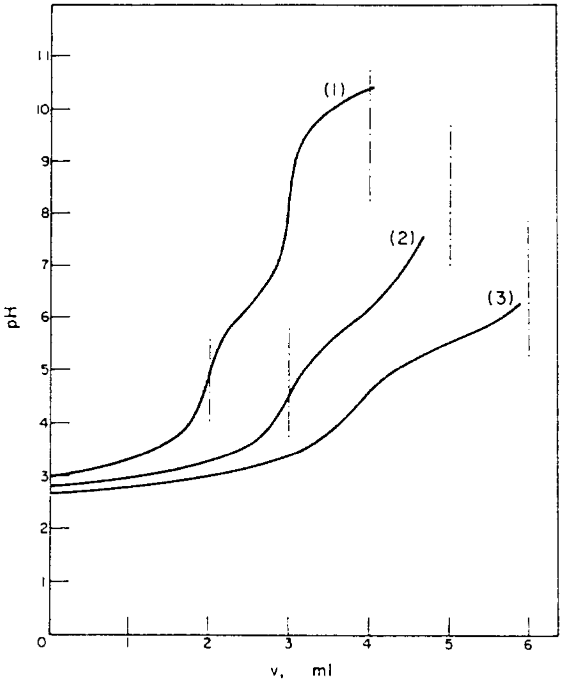


FIG. 1.—Titration curves of EDTA alone and in the presence of uranyl ion
(1) EDTA alone ($C_L = 10^{-3}M$) (2) with $UO_2{}^{2+}$ 1:1 ($C_L = C_M = 10^{-3}M$)
(3) with $UO_2{}^{2+}$ 2:1 ($C_L = 10^{-3}M$, $C_M = 2 \times 10^{-3}M$)

The last proton is attached to a non-co-ordinated nitrogen atom of EDTA and is titrated almost simultaneously.

Calculations carried out in accordance with this hypothesis gave satisfactory and reproducible results.

The behaviour of the curve for 2:1 mixtures of uranyl nitrate and EDTA suggests the formation of a $(UO_2)_2L$ complex; the inflexions at $v \sim 4$ ml and $v \sim 6$ ml require two further protons being titrated, which may again come from co-ordinated water molecules. Calculations carried out on this basis also gave satisfactory and reproducible results.

The constants obtained for the simple species are summarized in Table I.

The $UO_2{}^{2+}$—EDTA system has already been studied by several investigators, most of the work published being of a qualitative nature.[9,12]

Klygin, Smirnov and Nikol'skaya[13], Starý and Pašilova[14], Bhat and Krishnamurthy[15] gave numerical values for the constants of the equilibria involved, but the first authors identified just the 1:1 complex UO_2HL^-[13,14] and the last used a spectrophotometric method which necessitated some simplifying assumptions for the calculations to be possible. Agreement seems to have been reached on the structure of UO_2HL^- in which the ligand should have only one co-ordinated nitrogen atom.

TABLE I.—FORMATION CONSTANTS OF PROTON AND URANYL COMPLEXES OF EDTA (log K)
$T = 25{\cdot}0 \pm 0{\cdot}1$°C $\mu = 0{\cdot}100M$ (KNO_3)

Species	Constant	Value
HL^{3-}	log $K_1{}^H$	$10{\cdot}15 \pm 0{\cdot}01$
H_2L^{2-}	log $K_2{}^H$	$6{\cdot}18 \pm 0{\cdot}01$
H_3L^-	log $K_3{}^H$	$2{\cdot}69 \pm 0{\cdot}02$
H_4L	log $K_4{}^H$	$2{\cdot}0 \pm 0{\cdot}1$
$UO_2(H_2O)HL^-$	log K_{MHL}	$7{\cdot}40 \pm 0{\cdot}02$
$(UO_2)_2(H_2O)_2L$	log β_{M_2L}	$17{\cdot}87 \pm 0{\cdot}03$

The results obtained in the present work compare satisfactorily with those reported by the previous authors; hence, log $K_{MHL} = 7{\cdot}40$ for the complex $UO_2(H_2O)HL^-$ is in excellent agreement with the value obtained by Starý and Pašilova (log $K_{MHL} = 7{\cdot}32$) by using a solvent-extraction method.[14] The value determined by Bhat and Krishnamurthy with a spectrophotometric technique[15] is higher (log $K_{MHL} = 7{\cdot}96$) but of the same order of magnitude. For the 2:1 complex $(UO_2)_2(H_2O)_2L$, the same authors report log $\beta_{M_2L} = 18{\cdot}01$,[15] which is again in good agreement with the value that we have obtained (log $\beta_{M_3L} = 17{\cdot}87$), although slightly higher than this.

It should be remarked that Bhat and Krishnamurthy did not take into account the presence of $UO_2(H_2O)HL^-$ when calculating the constant of the 2:1 complex and assumed that only this species was formed under the conditions of the measurements. This assumption is not justified, as can be seen in a sample of our own calculations of β_{M_2L}, which included the concentrations of both $UO_2(H_2O)HL^-$ and $(UO_2)_2(H_2O)_2L$, denoted by MHL and M_2L respectively—Table II.

TABLE II.—CALCULATIONS FOR THE DETERMINATION OF log β_{M_2L}
$T = 25{\cdot}0 \pm 0{\cdot}1$°C, $\mu = 0{\cdot}100M$ KNO_3)

a	pH	[L] × 10^{15}	[M] × 10^4	[MHL] × 10^4	[M_2L] × 10^4	β_{M_2L} × 10^{-17}	log β_{M_2L}
0·500	2·683	0·775	7·239	4·027	2·666	6·564	17·82
1·100	2·774	1·042	6·381	3·870	3·132	7·381	17·87
1·300	2·810	1·171	6·141	3·853	3·247	7·353	17·86
1·400	2·830	1·251	6·049	3·873	3·276	7·157	17·86
1·500	2·850	1·330	5·896	3·833	3·366	7·279	17·86
1·600	2·869	1·405	5·716	3·757	3·488	7·599	17·88
1·700	2·890	1·495	5·547	3·696	3·596	7·817	17·89
1·800	2·914	1·610	5·422	3·681	3·658	7·729	17·89
1·900	2·940	1·751	5·382	3·743	3·640	7·177	17·86
2·000	2·961	1·840	5·056	3·520	3·909	7·301	17·86
2·500	3·121	2·956	4·622	3·577	4·064	6·435	17·81
3·000	3·342	5·237	3·447	2·843	4·985	8·012	17·90

log $\beta_{M_2L} = 17{\cdot}87 \pm 0{\cdot}03$.

The consistency of the results obtained in a ten-fold range of concentrations (log $\beta_{M_2L} = 17{\cdot}77$ for $C_M = 10^{-2}M$, $\mu = 1{\cdot}0M$ KNO_3) gives further support to our results, and it seems likely that if the actual concentration of the several species had been taken into account, Bhat and Krishnamurthy's constants would be lower, thus improving still further the agreement with the values presented in this work.

A different line of evidence comes from the comparison of the experimentally determined value of log β_{M_2L} with that predicted by the equation:

$$\log K_{ML} = 1{\cdot}19 \log K_{HL} - 1{\cdot}87$$

which was derived for 12 iminodiacetate ligands.[2]

For this case $\log K_{HL} = \log K_1{}^H + \log K_2{}^H = 10{\cdot}15 + 6{\cdot}18 = 16{\cdot}33$; hence, the predicted log β_{M_2L} is 17·56 ± 0·25, again in good agreement with the experimental value.

The same reasoning can be applied to the protonated complex $UO_2(H_2O)HL^-$, but now the constant predicted by the equation above is log K_{MHL} = 5·65 while the experimental value is log K_{MHL} = 7·40. This is rather unexpected and surprising, but comparison with the formation constants of similar complexes of closely related ligands confirms that EDTA is behaving rather abnormally in this case.

In Table III we present calculated and experimental values of log K_{MHL} for the uranyl complexes of 1,2-diaminocyclohexane-*N*,*N'*-tetra-acetic acid (DCTA), together with the corresponding values for EDTA.

TABLE III.—COMPARISON OF log K_{MHL} VALUES FOR THE URANYL COMPLEXES OF DCTA AND EDTA

Ligand	$pk^{H}_{H_2L}$	*expt.* log K_{MHL}	*calc.* log K_{MHL}	Δ
EDTA	6·18	7·40	5·48	+1·92
DCTA	6·12	5·27*	5·41	−0·14

* Ref. 14

The difference of behaviour in the two systems is obvious, implying that either EDTA is not acting only as a terdentate ligand towards the $UO_2{}^{2+}$ ion or that some other interaction between the ligand and this ion must be considered, besides co-ordination by the iminodiacetate moiety.

The first hypothesis is highly unlikely in view of the titration curves, consistency of results and synthetic work;[15] as to the second hypothesis, some further data for the corresponding complexes of other polyaminocarboxylate ligands will help the discussion.

In Table IV, we summarise the results obtained for 1,3-diaminopropanetetra-acetic acid (PDTA) and for 1,6-diaminohexanetetra-acetic acid (HDTA), together with those for DCTA and EDTA.

TABLE IV.—COMPARISON OF log K_{MHL} FOR THE URANYL COMPLEXES OF EDTA, PDTA, HDTA AND DCTA
$T = 25{\cdot}0 \pm 0{\cdot}1°C.$ $\mu = 0{\cdot}1M\ (KNO_3)$

Ligand	$pk^{H}_{H_2L}$	*expt.* log K_{MHL}	*calc.* log K_{MHL}	Δ
EDTA	6·18	7·40	5·48	+1·92
PDTA	7·88	8·94	7·51	+1·43
HDTA	9·75	9·96	9·73	+0·23
DCTA	6·12	5·27*	5·41	−0·14

* Ref. 14

The results presented in Table IV are quite significant and show that the abnormally high values of log K_{MHL} are related to the *closeness* of the two nitrogen atoms in the molecule of the ligands.

Thus, for EDTA, with two methylene groups between the nitrogen atoms, there is an increase of about 2·6 kcal/mole in the ligational free energy of the complex, whereas for PDTA, with three methylene groups separating the two nitrogen atoms, this increase is 2·0 kcal/mole. For HDTA, with six methylene groups between the nitrogen atoms and for DCTA in which the nitrogen atoms are *trans* relative to the cyclohexane nucleus, the deviation between experimental and calculated log K_{MHL} values is within the mean deviation of the predicted values, as one would expect if the ligands behave strictly as terdentate towards the UO_2^{2+} ion.

Now, since one of the nitrogen atoms of EDTA or PDTA is undoubtly protonated in the $UO_2(H_2O)HL^-$ complex, it is obvious that it cannot be involved in co-ordination to the metal and the reason for the abnormal stability of this species, which is related to the length of the chain between the nitrogen atoms, must be looked for in some other structural detail also related to the length of that chain.

Molecular models show that there is very little likelihood of a third carboxylate group co-ordinating to the uranium atom, whatever the distribution of the ligands in the equatorial plane of UO_2^{2+}, but support the possibility of hydrogen bonding between the protonated nitrogen atom in EDTA or PDTA and one oxygen atom in UO_2^{2+}, as schematically represented in Fig. 2.

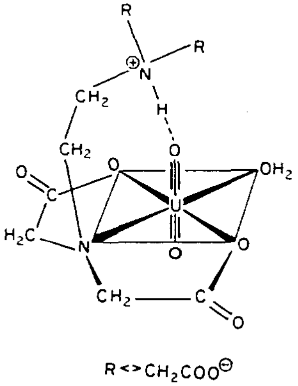


FIG. 2.—Hydrogen bonding in the $UO_2(H_2O)HL^-$ complex.

This is not possible in the DCTA chelate and not very likely in the complex formed by HDTA, except at the expense of considerable loss of configurational entropy of the ligand.

The formation of hydrogen bonds can account for the 2–3 kcal/mole increase in stability of the protonated complexes of EDTA as well as PDTA, and explains also the low ionization constant of the proton bound to nitrogen in these complexes, when compared with the "normal" value in the free ligand or in similar complexes of other ligands. The experimental demonstration of its existence is not, however, very easy, although the synthesis of well-defined species for spectroscopic studies, which is under way, may give some interesting evidence.

Olated species

The titration curves of Fig. 1 suggest the existence of a molecule which ionizes to form the hydroxo-complex $UO_2(OH)HL^-$. The remaining ionizable proton is attached to an unco-ordinated nitrogen atom of EDTA and dissociates at a pH lower than is usual for free ammonium radicals.

It is unlikely that a species such as $UO_2(OH)HL^-$ exists in solution except at comparatively high dilutions and one would expect polynuclear complex formation to take place, leading, in this case, to a dimer with two OH bridges. For the 2:1 complex, $(UO_2)_2(H_2O)_2L$, similar behaviour should lead to the formation of several polymers, since the olation reaction can take place at opposite ends of the complex molecule.

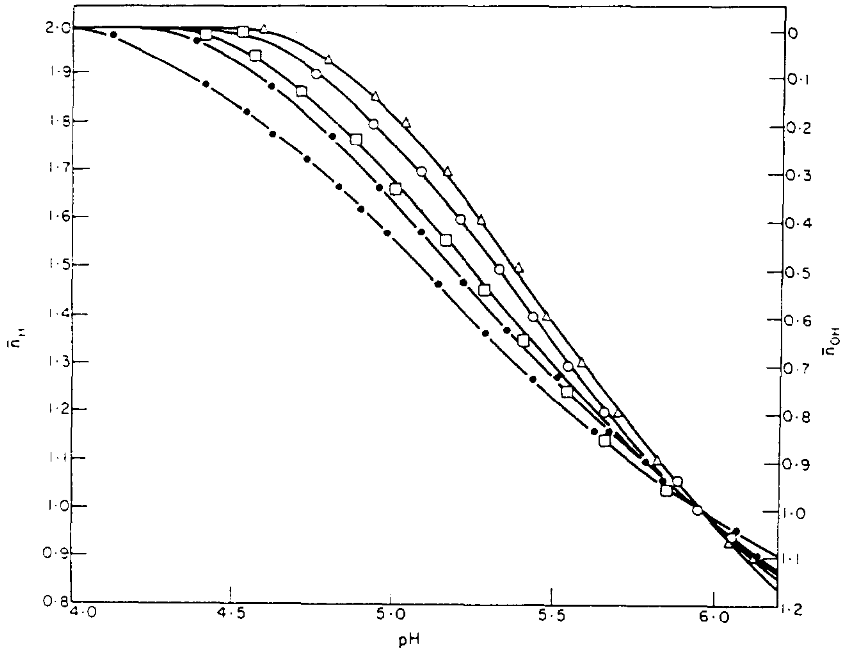


FIG. 3.—Formation curves for the olation of $UO_2(H_2O)HL^-$, initial concentration B.
△—$B = 5{\cdot}00 \times 10^{-4}M$ ○—$B = 1{\cdot}00 \times 10^{-3}M$
□—$B = 1{\cdot}92 \times 10^{-3}M$ ⊗—$B = 2{\cdot}46 \times 10^{-3}M$
●—$B = 4{\cdot}92 \times 10^{-3}M$

To test these possibilities and determine the formulae and formation constants of the various species formed, we have titrated 1:1 and 2:1 mixtures of UO_2^{2+} and EDTA over a ten-fold concentration range in 1·0*M* potassium nitrate media.

The titration data were plotted as $\bar{n}_H$ *vs.* pH curves and are presented in Figs. 3 and 4.

The formation function $\bar{n}_H$ is calculated by $\bar{n}_H = (2B - aB)/B = 2 - a$ where B is the total concentration of the 1:1 or 2:1 complexes and a is the degree of neutralization.

Although the use of $\bar{n}_{OH}$ instead of $\bar{n}_H$ would be in better agreement with the nature of the reaction, there is no advantage in this practice since the actual measured quantity is pH and conversions would be needed anyway.

The curves in Fig. 3 cross over at $\bar{n}_H = 1$, suggesting that only one polynuclear complex A_PB_Q co-exists with the mononuclear species, P/Q being equal to 1.

We have thus considered the physically obvious hypothesis of co-existence of the chelates $UO_2(H_2O)HL^-$, $UO_2(OH)HL^{2-}$, $(UO_2)_2(OH)_2H_2L_2{}^{4-}$ and their ionization products.

The normalized curve for this case has already been given by Sillén,[5] and Rossotti and Rossotti[6] and was adapted to the present case by considering $P = Q = 2$ and rearranging.

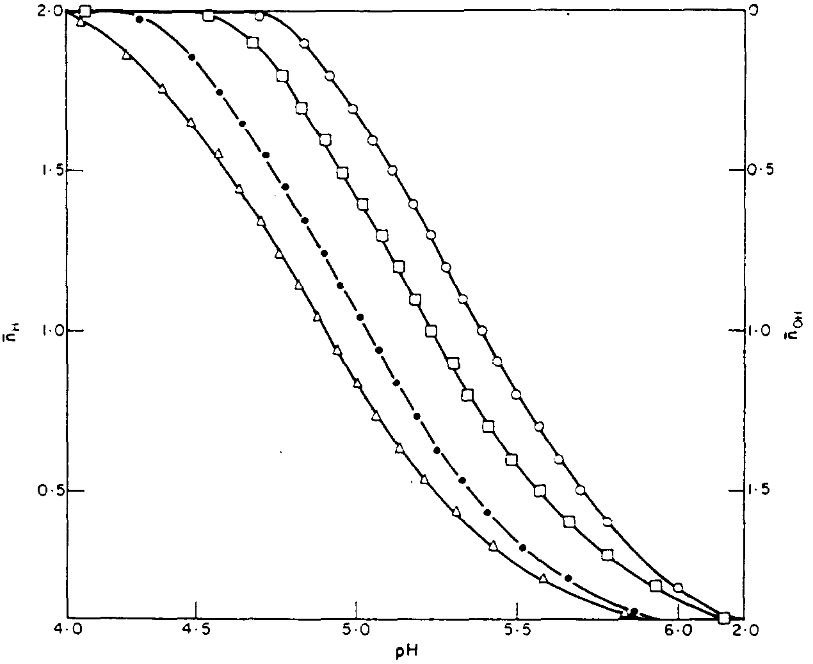


FIG. 4.—Formation curves for the olation of $(UO_2)_2(H_3O)_2L$, initial concentration B.
○—$B = 5{\cdot}00 \times 10^{-4}M$ □—$B = 1{\cdot}00 \times 10^{-3}M$
●—$B = 2{\cdot}46 \times 10^{-3}M$ △—$B = 4{\cdot}92 \times 10^{-3}M$

The actual expression used was

$$\log \mathbf{B} = \log[(\mathbf{a} + 2R\mathbf{a}^2) - \bar{n}(1 + \mathbf{a} + R\mathbf{a}^2)] + \log(2R\mathbf{a}^2 - 2) - 2\log \mathbf{a} - 2\log(2\bar{n} - 2)$$

The symbols have the meanings given by these authors,[5,6] and the best value for R, found by iteration, is 0·209.

In Fig. 5 the experimental data are superimposed on the normalized curves; the agreement is quite satisfactory and the formation constants can thus be obtained:

$$\beta_{11} = \frac{[UO_2(OH)HL]}{[UO_2(OH)L][H]} = 10^{6{\cdot}30}$$

$$\beta_{12} = \frac{[UO_2(H_2O)HL]}{[UO_2(OH)L][H]^2} = 10^{11{\cdot}92}$$

$$\beta_{22} = \frac{[(UO_2)_2(OH)_2H_2L_2]}{[UO_2(OH)L]^2[H]^2} = 10^{15{\cdot}87}$$

For the complex $UO_2(H_2O)HL^-$ we have then:

1st proton ionization constant (H_2O): $pk_1 = 5{\cdot}62$
2nd proton ionization constant ($^-NH^+$): $pk_2 = 6{\cdot}30$
dimerization constant: $\log K_D = 3{\cdot}27$
at $T = 25°$ and $\mu = 1{\cdot}0$ (KNO_3)

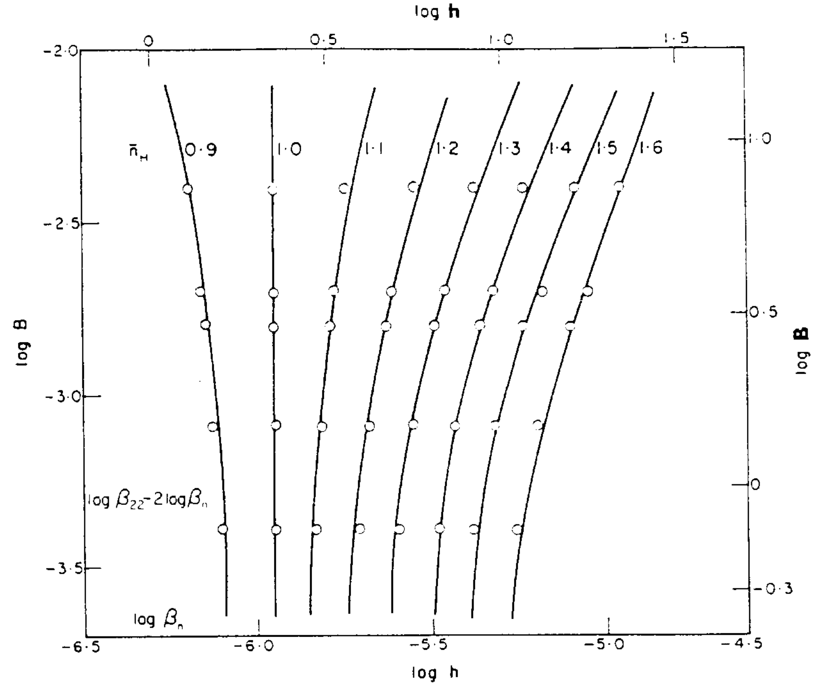


FIG. 5.—Olation of the complex $UO_2(H_2O)HL^-$; experimental points (log B, log h) superimposed on theoretical normalized curves (log **B**, log **h**) for various values of $\bar{n}_H$.

The dimerization constant K_D is defined as

$$K_D = \frac{[(UO_2)_2(OH)_2H_2L_2]}{[UO_2(OH)HL]^2}$$

It is of interest to compare these results with those reported by previous investigators who studied the uranyl complexes of some related ligands.

Thus Rajan and Martell[16] found for the uranyl chelate of *N*-hydroxyethyliminodiacetic acid $UO_2(H_2O)L'$, the values

ionization of co-ordinated water: $pk_1 = 5{\cdot}87$

dimerization constant: $\log K_D = 3{\cdot}65$

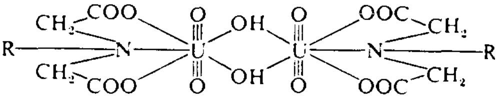
at the same temperature and ionic strength.

For the reaction

$$2UO_2(H_2O)L' \rightleftharpoons (UO_2)_2(OH)_2L'^{2-}_2 + 2H^+$$

these authors reported an equilibrium constant $K = 10^{-8.08}$; the equivalent reaction gives in our case $K' = 10^{-7.97}$.

The agreement is quite satisfactory and is evidence for the similarity of behaviour in both examples, implying similar structures for the dimers, as in **I** below:



I

where R = —CH_2—CH_2OH for *N*-hydroxyethyliminodiacetic acid and —CH_2—CH_2—$\overset{+}{N}H(CH_2COO^-)_2$ for EDTA.

As for the olation of 2:1 species, it can be seen that the curves in Fig. 4 have the same shape, within the limits of experimental error, and are only shifted along the log *h* axis. Moreover, the spacing Δ log *h* between two curves is proportional to log *B*:

$$\left(\frac{\partial \log B}{\partial \log h}\right)_{\bar{n}_H} = 2$$

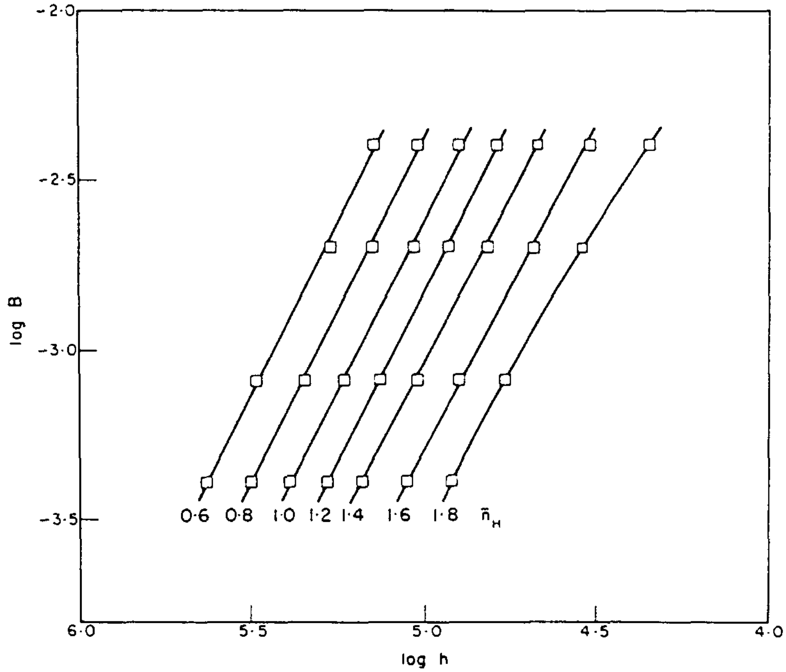


Fig. 6.— Olation of the complex $(UO_2)(H_2O)_2L$: variation of log *B* with log *h* for various values of $\bar{n}_H$. Constant slope *t*.

This is even more clear in Fig. 6, where log *B* is plotted as a function of log *h* for several values of $\bar{n}_H$.

If a "core + links" mechanism is admitted for the olation of the 2:1 complexes, the most probable general formulae for the resulting species will be[7,8]

$$[(UO_2)_2L(OH)_t]_n(OH)_r.2H_2O$$

TABLE V.—EQUILIBRIUM CONSTANTS OF URANYL COMPLEXES OF EDTA (H_4L)
$T = 25{\cdot}0 \pm 0{\cdot}1°C$ $\mu = 1{\cdot}00M$ (KNO_3)

Reactions	Constant	Value
$HL^{3-} + UO_2^{2+} \rightleftharpoons UO_2HL^-$	$\log K_{MHL}$	$7{\cdot}35 \pm 0{\cdot}02$
$L^{4-} + 2UO_2^{2+} \rightleftharpoons (UO_2)_2L$	$\log \beta_{M_2L}$	$17{\cdot}77 \pm 0{\cdot}04$
$UO_2(OH)L^{3-} + H^+ \rightleftharpoons (UO_2)(OH)HL^{2-}$	$\log \beta_{11}$	6·30
$UO_2(OH)HL^{2-} + H^+ \rightleftharpoons (UO_2)(H_2O)HL^-$	$\log K_{12}$	5·62
$UO_2(OH)L^{3-} + 2H^+ \rightleftharpoons (UO_2)(H_2O)HL^-$	$\log \beta_{12}$	11·92
$2UO_2(OH)L^{3-} + 2H^+ \rightleftharpoons (UO_2)_2(OH)_2H_2L_2^{4-}$	$\log \beta_{22}$	15·87
$2UO_2(OH)HL^{2-} \rightleftharpoons (UO_2)_2(OH)_2H_2L_2^{4-}$	$\log K_D$	3·27
$2UO_2(H_2O)HL^- \rightleftharpoons (UO_2)_2(OH)_2H_2L_2^{4-} + 2H^+$	pk	7·97
$2(UO_2)_2(H_2O)_2L \rightleftharpoons (UO_2)_4(H_2O)_2(OH)_2L_2^{2-} + 2H^+$	pk_1	7·38
$(UO_2)_2(H_2O)_2L[(UO_2)_2(OH)_2L]_{n-1}^{2(n-1)-} + (UO_2)_2(H_2O)_2L \rightleftharpoons (UO_2)_2(H_2O)_2L[(UO_2)_2(OH)_2L]_n^{2n-} + 2H^+$	pk	7·08

which can be abbreviated to

$$A_r(A_tB)_n.2H_2O$$

where A stands for (OH) and B for $(UO_2)_2L$.

In these conditions, according to Fig. 6 and since

$$\frac{\partial \log B}{\partial \log h} = -\frac{\partial \log B}{\partial \log [OH]}$$

the "core + links" mechanism will be such that

$$r = -t = -2$$

The general formula of the olated complexes will then be

$$(UO_2)_2L[(UO_2)_2(OH)_2L]_{n-1}.2H_2O \quad \text{or} \quad B[B(OH)_2]_{n-1}.2H_2O.$$

Since B, *e.g.*, $(UO_2)_2L.2H_2O$, predominates over all the other species at one end of the range of pH studied, the limits for $\bar{n}_H$ are $t + r/n_{min} = 0$ and $t + r/n_{max} = 2$, as derived from Fig. 4.

Hence $n_{min} = 1$ and $n_{max} = \infty$, which means that an unlimited series of complexes may be formed, corresponding to the general formula above.

By adoption of the three working hypotheses suggested by Sillén for the case of repeated reactions,[8] theoretical curves can be constructed and compared with the experimental curve drawn through the points $y = \bar{n}_H/2$, $x = \log B - t \log h$.

Very good agreement is obtained for the hypothesis of all consecutive constants being equal, which is to be expected from statistical considerations: see Fig. 7.

For this mechanism, the calculations give $k_1 = 0{\cdot}5 \times 10^{-7{\cdot}08} = 10^{-7{\cdot}38}$ for the reaction

$$2(UO_2)_2(H_2O)_2L \rightleftharpoons (UO_2)_4(H_2O)_2(OH)_2L_2^{2-} + 2H^+$$

and $k = 10^{-7.08}$ for the consecutive reactions corresponding to the general scheme

$$(UO_2)_2(H_2O)_2L[(UO_2)_2(OH)_2L]^{2(n-1)-}_{(n-1)} + (UO_2)_2(H_2O)_2L \rightleftharpoons$$
$$(UO_2)_2(H_2O)_2L[(UO_2)_2(OH)_2L]^{-2n}_{n} + 2H^+$$

with $n \geqslant 2$.

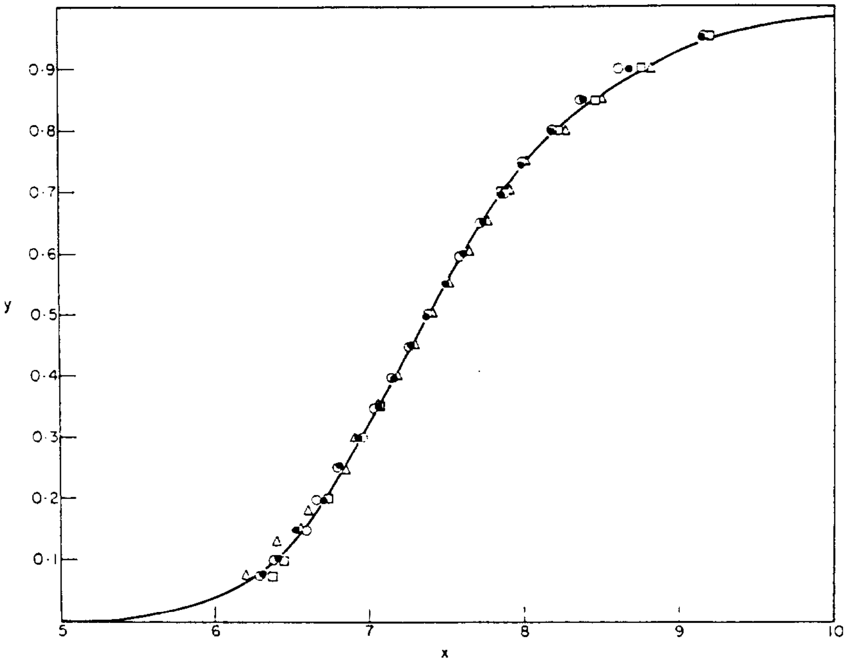


FIG. 7.—Olation of the complex $(UO_2)_2(H_2O)_2L$: experimental points ($y = \bar{n}_H/2$, $x = \log B - t \log h$) superimposed on the theoretical curve $y = f(x)$ for a "core + links" mechanism with equal consecutive constants (Sillén's hypothesis IIIa[8])

○—$B = 5{\cdot}00 \times 10^{-4}M$ □—$B = 1{\cdot}00 \times 10^{-3}M$
●—$B = 2{\cdot}46 \times 10^{-3}M$ △—$B = 4{\cdot}92 \times 10^{-3}M$

The constant k was obtained, as usual, from the deviation of the experimental from the theoretical curve, measured on the x axis for $y = 0{\cdot}5$, using the relationship $\log k = \log 2 - x_{0\cdot5}$.[8]

These results may be compared with those obtained by Ahrland, Hietanen and Sillén[17] for the hydrolysis of the UO_2^{2+} ion, which follows a similar mechanism. The reported constants are $k_1 = 10^{-6.05}$ and $k = 10^{-6.35}$ at 20° and $\mu = 1{\cdot}0M$ ($NaClO_4$).

Although the experimental conditions are not the same, the differences observed are within what one would expect, since hydrolysis of the UO_2^{2+}—EDTA species is less probable than that of UO_2^{2+} alone, on purely statistical grounds.

Again on statistical grounds one expects the constant k_1 for the reaction above to be 4 times the constant for the reaction

$$2UO_2(H_2O)HL^- \rightleftharpoons (UO_2)_2(OH)_2H_2L^{4-} + 2H^+$$

which is, as we have seen, $10^{-7.97}$; this follows from the possibility for the olation to take place at either side of the molecule in $(UO_2)_2(H_2O)_2L$ and only at one side in $UO_2(H_2O)HL$.

As a matter of fact $4 \times 10^{-7\cdot97} = 10^{-7\cdot37}$, in perfect agreement with the value we have determined, $10^{-7\cdot38}$, but it should be remarked that this is not the universal rule.

The structure of the olated polymers seems then to be similar to that given for the dimer of $UO_2(H_2O)HL^-$, extended in one dimension to form linear compounds. The attempts made to isolate some definite species failed; the products were always sheet-like crystalline masses but of variable composition. For the simple chelates, however, the preparative work of Bhat and Krishnamurthy, who synthesized $UO_2H_2L.H_2O$ and $(UO_2)_2L$. $4H_2O$, confirms the structures suggested.

All the results obtained in the present work are summarized in Tables I ($\mu = 0\cdot100M$ KNO_3) and V ($\mu = 1\cdot00M$ KNO_3).

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Zusammenfassung—Die Uranylkomplexe von EDTA wurden potentiometrisch untersucht; die Stabilitätskonstanten der Chelate mit Metall: Ligand -Verhältnis 1:1 und 1:2 wurden bestimmt sowie die entsprechenden Hydrolysen- und Polymerisationskonstanten. Mögliche Strukturen dieser Spezies werden diskutiert. Zur Erklärung der abnormal hohen Stabilität von $UO_2(H_2O)HL^-$ wird eine Wasserstoffbrücke zwischen einem protonierten Stickstoffatom des Liganden und einem Sauerstoffatom von UO_2^{2+} vorgeschlagen.

Résumé—On a étudié par potentiométrie les complexes uranyles de l'EDTA; on a déterminé les constantes de stabilité des chélates 1:1 et 2:1 (rapport métal-ligand), ainsi que les constantes respectives d'hydrolyse et de polymérisation. On discute de structures possibles pour ces espèces. Pour interpréter la stabilité anormalement grande de $UO_2(H_2O)HL^-$, on suggère une liaison hydrogène entre un atome d'azote protoné du ligand et un atome d'oxygène de UO_2^{2+}.

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MOLYBDÄN(VI)-HYDROXYLAMIN-KOMPLEXE—III

DIE CHELOMETRISCHE BESTIMMUNG VON MOLYBDÄN ALS TERNÄRER MOLYBDÄN(VI)-HYDROXYLAMIN-ÄDTA-KOMPLEX UND VERGLEICH DES VERFAHRENS MIT DER BEREITS BEKANNTEN TITRIERMETHODE VON MOLYBDÄN(V) MIT ÄDTA

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Zusammenfassung—Es erfolgt eine eingehende Untersuchung der Molybdäntitration über den Molybdän(V)-Hydroxylamin-ÄDTA-Komplex hinsichtlich Bildungsbedingungen, Rücktitrierverfahren, Störungen durch Fremdionen, Reproduzierbarkeit und Richtigkeit. Den Abschluß bildet ein kritischer Vergleich der Methode mit dem chelometrischen Verfahren, welches die Bildung des Mo(V)-ÄDTA-Komplexes ausnützt.

Die chelometrische Titration des Molybdäns konnte bislang in der Praxis nur unter Ausnutzung des dimeren Mo(V)-ÄDTA-Chelats mit Erfolg angewandt werden. Eine umfassende Literaturübersicht, die einschlägigen Arbeiten betreffend, wurde kürzlich veröffentlicht.[1] Ein Nachteil dieses Verfahrens im Vergleich zu den meisten übrigen chelometrischen Titrationen anderer Kationen ist der ungünstigere stöchiometrische Umrechnungsfaktor, verursacht durch die Bildung eines Chelonats, das pro ÄDTA-Molekül zwei Molybdänatome enthält. Recht überraschend war es daher, daß Yaguchi und Kajiwara[2] kürzlich über eine Titrationsmethode berichteten, der die Bildung eines Mo(V)-ÄDTA-Komplexes mit einem Mo:ÄDTA-Verhältnis von 1:1 zugrunde lag. Die Autoren verwendeten lediglich anstatt des sonst üblichen Hydrazins Hydroxylamin als "Reduktionsmittel" für das Molybdän. Dieses überraschende Ergebnis veranlaßte uns zu umfangreichen Untersuchungen in dieser Richtung und in den beiden ersten Teilen[4,5] dieser Veröffentlichungsserie konnte bereits folgendes eindeutig bewiesen werden:

Molybdän(VI) wird von Hydroxylamin (Hy) *nicht* reduziert, sondern komplex gebunden wobei gleichzeitig Depolymerisation eintritt. Dieser Mo(VI)-Hy-Komplex ist befähigt mit Chelatbildnern insbesondere auch mit Chelonen ternäre Komplexe vom Typ Mo(VI):Hy:ÄDTA = 1:1:1 zu bilden. Und damit war bereits bewiesen, daß Yaguchi and Kajiwara[2] nicht fünfwertiges, sonders sechswertiges Molybdän titriert hatten.

Von diesen Erfahrungen ausgehend haben wir im weiteren die von den japanischen Autoren mitgeteilte Titrationsmethode genauer untersucht und sie vor allem mit der seinerzeit von Lassner und Scharf[3] eingeführten Titration von Mo(V) mit ÄDTA verglichen. Die Ergebnisse dieser Untersuchungen werden im folgenden mitgeteilt.

Bildungsbedingungen für das Mo(VI)-Hy-ÄDTA-Chelat

Die quantitative Bildung des Mo(VI)-Hy-ÄDTA-Komplexes erfolgt durch Sieden der mit Hydroxylamin und ÄDTA versetzten Molybdänlösung. Sie hängt in starkem

Maße von der Hydroxylaminkonzentration der Lösung und weit weniger vom molaren Verhältnis Mo(VI):Hy ab, soferne von vornherein für einen molaren Hydroxylaminüberschuß gesorgt ist. Die Werte der Tabelle I mögen dabei zur näheren Erläuterung dienen. Wie ersichtlich, erzielt man erst 100%ige Komplexierung des Molybdäns bei einer Hydroxylaminkonzentration von 1–2 g/100 ml, was beim Arbeiten im Volumen von 100 ml einem 24–29-fachen molaren Überschuß gleichkommt. Andererseits kann man auch mit einem 10-fachen molaren Überschuß das Auslangen finden und 100 %ige Komplexbildung erreichen, wenn man in einem Volumen von 8 ml arbeitet. Dies entspricht aber umgerechnet wiederum einer Hydroxylaminkonzentration von etwa 1 g/100 ml. Ist jedoch einmal quantitative Komplexbildung erfolgt, so kann man die Lösung ohne weiteres verdünnen ohne daß dabei eine wesentliche Dissoziation festzustellen ist. Dies deutet auf eine hohe *kinetischeqe* Stabilität des Komplexes hin.

TABELLE I.—ABHÄNGIGKEIT DER KOMPLEXBILDUNG Mo–Hy–ÄDTA VON DER HYDROXYLAMINKONZENTRATION

Molares Verhältnis Mo:Hy bei 100 ml Lösungsvolumen	Hydroxylaminkonzentration, *mg/100 ml*	Durch Titration ermittelter Anteil an gebildetem Mo–Hy–ÄDTA, %
1:5	41	~50
1:10	82	~70
1:24	1000	100
1:49	2000	100

(Molybdänmenge = 2 ml 0,05 m Lösung).

Entsprechend unseren Erfahrungen ist es am besten, die molybdänhaltige Lösung zuerst mit einem Hydroxylaminüberschuß zu versetzen, wobei die Hydroxylaminkonzentration nicht unter 1 g/100 ml liegen soll, und anschließend auf einen pH-Wert zwischen 2 und 5 zu bringen. Sodann wird bis zum Sieden erhitzt, ein gemessener Überschuß an ÄDTA-Standardlösung zugesetzt und weitere 15 Minuten am Sieden gehalten. Läßt man die Reaktion mit Hydroxylamin in stärker saurer Lösung ablaufen (0,5–1,0 n), so erhält man nach unseren Erfahrungen Unterwerte. Dies steht im Gegensatz zur Veröffentlichung von Yaguchi und Kajiwara.[2]

Rücktitration

Da die Reaktionsgeschwindigkeit von Mo-Hy + ÄDTA sehr gering ist (15 Minuten Sieden!) kann nur ein Rücktitrationsverfahren zur Bestimmung herangezogen werden. Yaguchi und Kajiwara geben an, daß man die Rücktitration des ÄDTA-Überschusses entweder bei pH 2 mit Wismutlösung gegen Xylenolorange oder bei pH 4,5 mit Kupferlösung gegen PAN vornehmen kann. Wir haben beide Methoden untersucht und festgestellt, daß sie vergleichbare Resultate liefern. Wir verwendeten lediglich anstatt Xylenolorange Methylthymolblau als Indikator bei der Rücktitration mit Wismut. Bei beiden Verfahren sind jedoch einige wichtige, unbedingt erwähnenswerte Feststellungen gemacht worden:

1) Die Rücktitration mit Wismutlösung funktioniert nur dann gut, wenn man in etwa 80° heißen Lösungen arbeitet. Infolge der Anwesenheit von Chlorid- bzw. Sulfationen (Hydroxylaminchlorid oder -sulfat) kommt es bei Wismutüberschuß

zur Bildung kolloidaler Formen, die bei Zimmertemperatur nur sehr zögernd mit der zugesetzten ÄDTA-Lösung bzw. mit dem Indikator reagieren.

2) Beim Rücktitrieren tritt bei Wismutüberschuß eine Verdrängungsreaktion ein:

$$\text{Mo–Hy–ÄDTA} + \text{Bi}^{3+} \rightarrow \text{Mo–Hy} + \text{Bi–ÄDTA}$$

Das Ausmaß dieser Reaktion ist einerseits von der Konzentration der freien Wismutionen und zum anderen von der Zeitdauer, während der sie wirksam (nicht an ÄDTA gebunden) sind, ab. Die bei einer "Pendeltitration" (mehrmalige Endpunktseinstellung mit Bi- und ÄDTA-Maßlösung) erhaltenen Ergebnisse in Tabelle II zeigen diesen Verdrängungseffekt recht deutlich. Beim Rücktitrieren ist daher darauf zu achten, daß man nur möglichst geringen Wismutüberschuß anwenden darf und diesen auch möglichst schnell wieder mit ÄDTA-Lösung zu kompensieren hat.

TABELLE II.—VERDRÄNGUNG VON Mo–Hy AUS DEM ÄDTA-CHELAT DURCH Bi^{3+}-IONEN

	ml 0,05 m ÄDTA *verbraucht*
1. Endpunktseinstellung	9,73
2. Endpunktseinstellung 30 sec nach Zugabe eines geringen Bi-Überschusses	9,71
3. Endpunktseinstellung 60 sec nach Zugabe eines geringen Bi-Überschusses	9,67
4. Endpunktseinstellung 120 sec nach Zugabe eines größeren Bi-Überschusses (1 ml 0,05 m Lösung)	9,54

(Theoretischer ÄDTA-Verbrauch = 9,73 ml 0,05 m Lösung).

3) Die Rücktitration mit Kupfermaßlösung bei pH 4,5 gegen PAN gelingt in der Hitze (70–80°) sehr gut. Es ist lediglich darauf zu achten, daß ein größerer Kupferüberschuß (etwa 0,5 ml 0,05 m Lösung) vermieden werden soll. Bei größerem Überschuß kommt es anscheinend ebenfalls zu einer Verdrängung. Mo–Hy wird durch Kupferionen aus dem ÄDTA-Chelat gedrängt. Dies ist daran erkenntlich, daß sich der Indikator schwach violett färbt und diese Färbung sowohl bei Kupfer als auch bei ÄDTA-Überschuß beibehält. Der Indikator ist "blockiert". Diese Erscheinung läßt auf die Bildung eines kinetisch stabilen Komplexes zwischen Mo-Hy und PAN schließen.*

Störungen durch Fremdionen

Der Umstand, daß die Titration bei pH 2 durchführbar ist gewährleistet bereits ein gewisses Maß an Selektivität, da bei diesem pH Chelonate mit geringer Stabilität ($pK < 15$) weitgehend dissoziiert sind. Metallionen mit höherer Chelonatstabilität wirken störend und müssen daher abgetrennt werden. Eine Ausnahme stellen lediglich alle diejenigen Kationen dar, deren ÄDTA-Chelate durch Fluorid zerlegbar sind. Sie können durch Fluoridzusatz *nach* erfolgter Mo(VI)–Hy–ÄDTA-Bildung gegenüber

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* Die Reaktionen von Mo-Hy mit metallochromen Indikatoren sind Gegenstand laufender Untersuchungen und es soll in Kürze darüber genauer berichtet werden.

ÄDTA maskiert werden. Fluoridzugabe vor der Komplexierung des Molybdäns wirkt störend, da quantitative Chelonatbildung verhindert wird.

Weinsäure, die im sauren Bereich häufig zur Maskierung von leicht hydrolysierbaren Ionen bei ÄDTA-Titrationen verwendet wird, stört ebenfalls und darf nicht anwesend sein.

Wolfram, welches an und für sich nur ein sehr instabiles ÄDTA-Chelat zu bilden vermag stört ebenfalls. Während der Reaktion mit Hydroxylamin werden die zwischen Wolfram und Molybdän gebildeten Heteropolyionen zu "Molybdänblau" reduziert. Bereits ein äquimolarer Gehalt an Wolfram führt zu unvollständiger Komplexierung des Molybdäns (etwa 97%), während bei fünffachem molarem Wolframüberschuß nurmehr 95% der vorgelegten Molybdänmenge gefunden werden konnten. Darüber hinaus ist der Indikatorumschlag am Titrationsendpunkt in Gegenwart von Wolfram sehr unscharf, während er sich bei reinen Molybdänlösungen auf Hundertstel Milliliter 0,05 m ÄDTA-Lösung festlegen läßt.

Reproduzierbarkeit

Aus einer Reihe von Einzelergebnissen haben wir die Standardabweichung für die Bestimmung von Molybdänmengen zwischen 10 und 50 mg errechnet: $s = \pm 0{,}03$ mg Molybdän. Die Versuche wurden mit reiner Molybdänlösung unter Verwendung von 0,05 m Maßlösungen (Bi^{3+} und ÄDTA) durchgeführt. Bei jedem Versuch wurde der Endpunkt durch "Pendeln" dreimal eingestellt und der Mittelwert dieser drei Messungen gebildet.

Richtigkeit

Unter Verwendung derselben Maßlösungen für beide Titrationsmethoden konnten wir feststellen, daß die Methode mit Hydroxylamin im Vergleich zu der seinerzeit von Lassner und Scharf[3] für Mo(V) mitgeteilten, konstant Unterbefunde von etwa 9–10% liefert. Daß die Titration von Mo(V) mit ÄDTA richtige Ergebnisse liefert, wurde schon seinerzeit[3] und weiters durch eine Reihe darauf folgender Arbeiten[1] bewiesen. Ein empirischer Faktor (Titerstellung der ÄDTA-Lösung mit einer Mo-Lösung bekannter Konzentration) ist daher bei Verwendung des Hydroxylaminverfahrens unbedingt erforderlich.

Vergleich mit der Methode von Lassner und Scharf[3]

1. Der Mo–Hy–ÄDTA-Komplex besitzt geringere Eigenfarbe, als das Mo(V)–ÄDTA-Chelat. Dies ist von Vorteil, da der Indikatorumschlag am Titrationsendpunkt besser wahrnehmbar ist.
2. Das Verhältnis von Mo:ÄDTA im Komplex ist 1:1 im Gegensatz zum Mo(V)–ÄDTA-Komplex, bei dem es 2:1 beträgt. Der stöchiometrische Umrechnungsfaktor ist daher beim Hydroxylaminkomplex günstiger.
3. Den in Punkt 1 und 2 aufgezeigten Tatsachen zufolge war für das Hydroxylaminverfahren eine bessere Reproduzierbarkeit zu erwarten. Für die Titration über das Mo(V)-ÄDTA-Chelat beträgt die, unter denselben Bedingungen wie sie oben für das Mo(VI)-Hy-ÄDTA-Verfahren beschrieben wurden ermittelte Standardabweichung $\pm$ 0,06 mg Molybdän. Sie ist also in der Tat doppelt so hoch, als die des Hydroxylaminverfahrens.
4. Nachteile gegenüber der Titration des fünfwertigen Molybdäns sind vor allem:

Der empirische Umrechnungsfaktor, die geringere Selektivität, wobei insbesondere die Störung durch Wolfram nachteilig ist. Bekanntermaßen gibt es nur wenige Möglichkeiten Molybdän neben Wolfram ohne vorhergehende Trennung schnell und exakt zu bestimmen. Letztlich ist noch als weiterer Nachteil die geringere Komplexstabilität anzuführen. Wie weiter oben gezeigt werden konnte, kommt es durch Kupfer- oder Wismutionen zu Verdrängungsreaktionen. Der Mo(V)–ÄDTA-Komplex hingegen ist thermodynamisch so stabil, daß er bei pH 2 Wismutionen teilweise aus dem ÄDTA-Chelat zu drängen vermag.

VERZEICHNIS DER IM TEXT VERWENDETEN ABKÜRZUNGEN

Mo(VI)	sechswertiges Molybdänpartikel ohne Berücksichtigung etwa vorhandener Aquo oder Hydroxoliganden
Mo(V)	fünfwertiges Molybdänpartikel ohne Berücksichtigung etwa vorhandener Aquo oder Hydroxoliganden
Hy	Hydroxylamin
ÄDTA	Äthylendiamin-*N*,*N*,*N′*,*N′*-tetraessigsäure
Mo(VI)–Hy	Molybdän(VI)–Hydroxylaminkomplex
Mo(VI)–Hy-ÄDTA	ternärer Molybdän(VI)–Hydroxylamin–ÄDTA-Komplex
Mo(V)–ÄDTA	dimerer Molybdän(V)–ÄDTA-Komplex
Xylenolorange	3,3′-Bis(*N*,*N*-di(carboxymethyl)-aminomethyl -*o*-Kresolphthalein
Methylthymolblau	Na-Salz von 3′3″-Bis-{[bis(carboxymethyl)amino]methyl}-5′5″-diisopropyl-2′2″-dimethylphenol-sulphonphthalein
PAN	1-(2-Pyridylazo)-2-naphthol

Summary—The titration of molybdenum *via* the molybdenum(VI)–hydroxylamine–EDTA complex is studied in detail. Formation conditions, a back-titration, interferences by foreign ions, precision and accuracy are discussed. This method is critically compared with the chelometric method based on the formation of the Mo(V)–EDTA complex.

Résumé—On étudie en détail le dosage du molybdène au moyen du complexe molybdène(VI)–hydroxylamine–EDTA. On discute des conditions de formation, d'un titrage en retour, des interférences d'ions étrangers, de la précision et de l'exactitude. Cette méthode est comparée de façon critique à la méthode chélatométrique basée sur la formation du complexe Mo(V)–EDTA.

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POLAROGRAPHIC AND POTENTIOMETRIC DETERMINATION OF THE STABILITY CONSTANTS OF LEAD, CADMIUM AND ZINC COMPLEXES WITH DITHIOCARBAMINOACETIC ACID

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Summary—The stability constants of lead, cadmium and zinc dithiocarbaminoacetic acid (TCA) complexes have been determined. Lead and cadmium TCA complexes were studied by means of a polarographic method. A competitive polarographic method was used for the study of zinc TCA complexes. Zinc and cadmium TCA complexes were also studied potentiometrically with an amalgam electrode. The stability constants found were: lead, log $\beta_2 = 13{\cdot}2$; cadmium, log $\beta_1 = 5{\cdot}4$ (pot.), log $\beta_2 = 9{\cdot}3$ (pot.), log $\beta_3 = 13{\cdot}7$ (pot.), 13·6 (pol.); zinc, log $\beta_1 = 3{\cdot}4$ (pot.), $<3{\cdot}8$ (pol.), log $\beta_2 = 6{\cdot}6$ (pot.), 6·4 (pol.), log $\beta_3 = 8{\cdot}9$ (pot.), 9·3 (pol.).

DITHIOCARBAMINOACETIC ACID ($NH_4S_2CNHCH_2CO_2NH_4 \cdot H_2O$; TCA) forms very stable water-soluble complexes with a number of metal ions,[1–3] and so can be used as a new masking agent in complexometry.[4] Knowledge of the stability constants will extend the applications of TCA in analytical chemistry. In our previous papers the acid dissociation constants of TCA[5] as well as the stability constants of cobalt(II)–TCA[6] and lead–TCA[7] complexes have been reported. The present paper deals with the determination of the stability constants of lead, cadmium and zinc complexes with TCA, by polarographic and potentiometric methods.

EXPERIMENTAL

Symbols[8]

A = total concentration of ligand A.
a = concentration of free ligand.
B = total concentration of central group B.
b = concentration of free central group.
n = number of ligands in mononuclear complex BA_n.
N = maximum coordination number.
$\bar{n} = (A - a)/B$ = average number of ligands A bound to one central group B.
$\alpha_c = [BA_c]/B$ = fraction of B in form of BA_c.
$\beta_n = [BA_n]/ba^n$ = over all stability constant.
z = number of electrons involved in reduction couple.
D = diffusion coefficient of species indicated by subscript.

Polarographic studies

Apparatus

Measurements were carried out with polarographic equipment including three electrodes according to Kolthoff and Lingane[9] (see Fig. 1). The following galvanic cell was used:

$Hg{-}Hg_2Cl_2$	satd. KCl soln.	$0{\cdot}2M$ KNO_3	$0{\cdot}05M$ formate buffer xM $B(NO_3)_n$ yM TCA zM KNO_3	dropping mercury electrode

The apparatus was prepared for measurements as follows: the vessel s was filled with a solution of known concentration B. The left-hand side of the bridge was filled with saturated potassium chloride solution by means of the vessel k and the stop-cock l, the right-hand side of the bridge was filled with $0{\cdot}2M$ potassium nitrate through the vessel b and the stop-cock m. Just before measurements were started the stop-cocks c and d were opened. The vessel s with the electrodes was kept in an air-thermostat at $25 \pm 0{\cdot}2°$. The solution in the vessel s was stirred with a magnetic stirrer and a stream of very pure nitrogen (99·999 %) was passed through it. Portions of the solution of the ligand were added from a microburette.

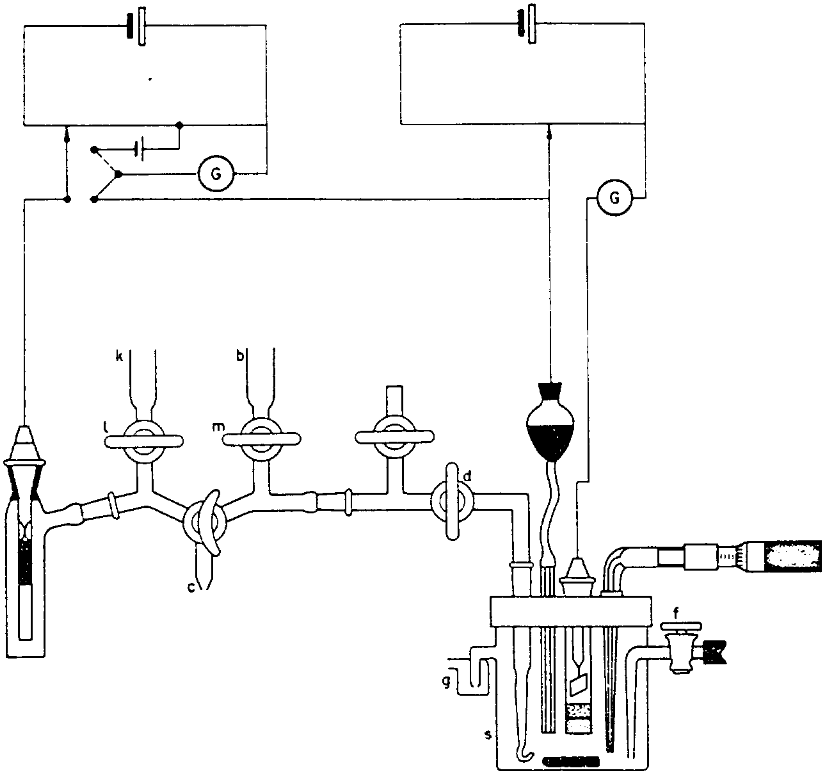

FIG. 1.—The apparatus for polarographic study of metal–TCA complexes.

The potential of the dropping mercury electrode was measured with a potentiometer with a precision of $\pm 0{\cdot}1$ mV (see the upper left-hand side in Fig. 1). The LP-55 polarograph is shown in the upper right-hand side of the same figure.

Procedure

First the reversibility of the electrode reaction was proved by means of the following criteria: (*i*) the half-wave potential does not depend on the depolarizer concentration and capillarity constants; (*ii*) the dependence log $i/(i_d - i)$ *vs.* E is linear with a slope equal to the theoretical value; (*iii*) the half-wave potentials of the cathodic and anodic waves (cadmium amalgam was used) are identical. Criterion (*ii*) is not decisive if the complexes are very strong and the ligand concentration is too low.[10]

Reversible polarographic waves for lead–TCA and cadmium–TCA complexes were obtained only with a high excess of the ligand, which is why only the overall stability constants for maximum co-ordination number were determined. The measurements were carried out under the following conditions: constant concentration of metal ion $5 \times 10^{-4}M$, varying concentration of TCA from 4×10^{-3} to $1 \times 10^{-1}M$; $5 \times 10^{-2}M$ formate buffer; constant ionic strength $\mu = 0{\cdot}2$, maintained with a corresponding concentration of potassium nitrate. Values of half-wave potentials at different ligand concentrations were read from the plots of log $i/(i_d - i)$ *vs.* E and values of $\Delta E_{1/2}$ were then computed with a precision of ± 1 mV. The $\Delta E_{1/2}$ values were used to calculate the over-all stability constants for maximum co-ordination number, from the equation

$$\Delta E_{1/2} = \frac{RT}{zF}\ln\sqrt{\frac{D_B}{D_A}} - \frac{RT}{zF}\ln\beta_N - N\frac{RT}{zF}\ln a. \tag{1}$$

Because in the range of concentrations used the approximation $a = A$ is not valid, the free ligand concentration a must be known to operate with equation (1). It was determined from the expression

$$a = A - N'B \tag{2}$$

where N' is the slope of the experimental plot $\Delta E_{1/2}$ *vs.* log A (Fig. 2—black circles) and represents the maximum co-ordination number [see equation (1)]. By the method of successive approximations the correct relationship $\Delta E_{1/2}$ *vs.* log a was found (Fig. 2—open circles). Then the values of the conditional stability constants β_N for lead and cadmium were obtained as the intercept of the plot $\Delta E_{1/2}$ *vs.* log a. The results are presented in Table VI. Some experimental data for lead and cadmium TCA complexes are shown in Tables I and II.

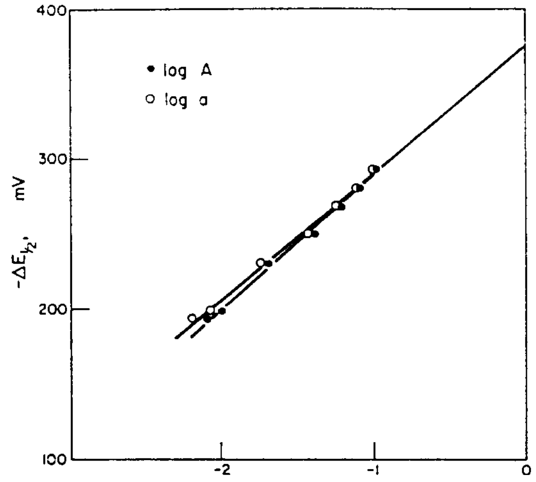

FIG. 2.—Dependence of $\Delta E_{1/2}$ on the concentration of TCA for the cadmium-TCA system.

TABLE I.—DATA FOR LEAD-TCA COMPLEXES, OBTAINED FROM ONE POLAROGRAPHIC EXPERIMENT

$\Delta E_{1/2}$, *mV*	*A*, *M*	log *A*	log a_1	log a_2	log α_0	a_2, *M*
−194·0	4×10^{-3}	−2·398	−2·585	−2·550	−6·36	$2{\cdot}83 \times 10^{-3}$
−207·8	6×10^{-3}	−2·222	−2·328	−2·316	−7·35	$4{\cdot}83 \times 10^{-3}$
−217·8	8×10^{-3}	−2·097	−2·174	−2·166	−7·68	$6{\cdot}83 \times 10^{-3}$
−223·0	1×10^{-2}	−2·000	−2·060	−2·054	−7·85	$8{\cdot}83 \times 10^{-3}$
−250·3	2×10^{-2}	−1·699	−1·728	−1·724	−8·80	$1{\cdot}88 \times 10^{-2}$
−270·0	4×10^{-2}	−1·398	−1·412	−1·410	−9·47	$3{\cdot}88 \times 10^{-2}$
−285·0	6×10^{-2}	−1·222	−1·232	−1·230	−10·00	$5{\cdot}88 \times 10^{-2}$
−292·3	8×10^{-2}	−1·097	−1·104	−1·104	−10·25	$7{\cdot}88 \times 10^{-2}$

Conditions: $B = 5 \times 10^{-4}M$ Pb(NO$_3$)$_2$; 0·05*M* formate buffer, pH 4·00 ± 0·05; 0·008% gelatine; volume 25 ml; ionic strength $\mu = 0{\cdot}2$ (KNO$_3$); temperature 25 ± 0·2°C; titrated with 1*M* TCA.

It was impossible to determine the stability constants of zinc-TCA complexes by this method, because of the irreversibility of the polarographic waves obtained. The stability constants of zinc were determined by means of a competitive method. To a solution containing lead ions and a large

Table II.—Data for cadmium–TCA complexes, obtained from one polarographic experiment

$\Delta E_{1/2}$, *mV*	*A*, *M*	log *A*	log *a*	log α_0	*a*, *M*
−193·5	8×10^{-3}	−2·097	−2·187	−6·55	$6{\cdot}50 \times 10^{-3}$
−198·8	1×10^{-2}	−2·000	−2·070	−6·73	$8{\cdot}50 \times 10^{-3}$
−231·0	2×10^{-2}	−1·699	−1·732	−7·84	$1{\cdot}85 \times 10^{-2}$
−251·5	4×10^{-2}	−1·398	−1·414	−8·50	$3{\cdot}85 \times 10^{-2}$
−269·5	6×10^{-2}	−1·222	−1·233	−9·11	$5{\cdot}85 \times 10^{-2}$
−281·3	8×10^{-2}	−1·097	−1·105	−9·52	$7{\cdot}85 \times 10^{-2}$
−293·5	1×10^{-1}	−1·000	−1·006	−9·94	$9{\cdot}85 \times 10^{-3}$

Conditions as for Table I, with $B = 5 \times 10^{-4}M$ Cd(NO$_3$)$_2$.

excess of ligand, increasing amounts of zinc were added. For every concentration of zinc the shift of the half-wave potential of the lead–TCA complex was measured, and then by using the equation[8]

$$\Delta E_{1/2} = \frac{RT}{zF}\left(\ln \alpha_0 + \ln \frac{(i_d)_{A=0}}{(i_d)_A}\right) \tag{3}$$

the value of α_0 was computed. The value of log *a* was graphically read from the plot of log α_0 *vs* log *a* for the lead–TCA complex. The function $\bar{n}_{Zn}$ *vs*. *a* was calculated by using the equation

$$\bar{n}_{Zn} = \frac{A - a - \bar{n}_{Pb}B_{Pb}}{B_{Zn}}. \tag{4}$$

The formation curve for the zinc–TCA complex, obtained from many experiments, is shown in Fig. 3, where the full curve is the theoretical curve computed from the experimentally obtained conditional stability constants for zinc, and the points are the experimental data. The data $\bar{n}(a)$ were treated by Rossotti's graphic method[8] (Figs. 4 and 5). Experimental results from a single experiment are shown in Table III.

POTENTIOMETRIC STUDIES

In the potentiometric study measurements were carried out with apparatus similar to that previously described.[7]

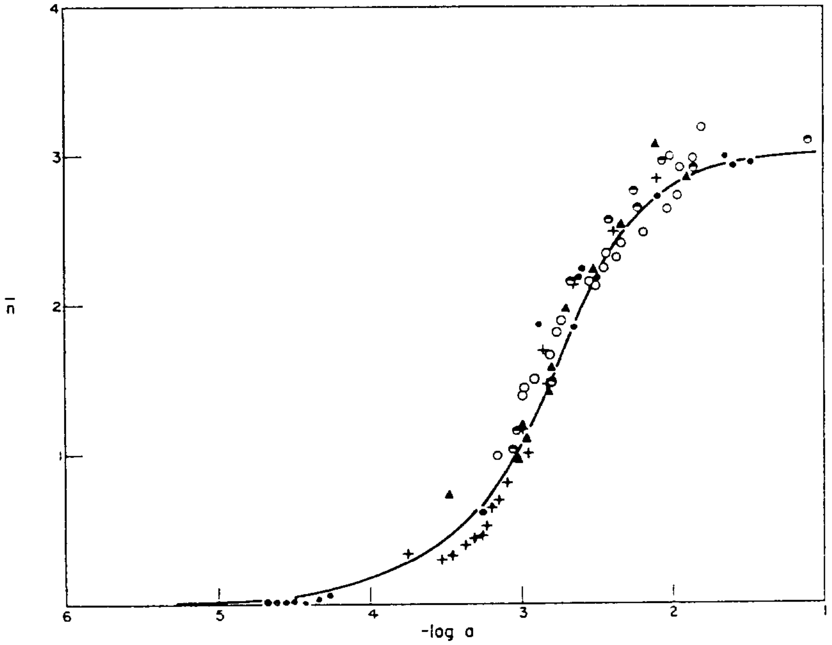

Fig. 3.—Formation curve of zinc–TCA complexes.

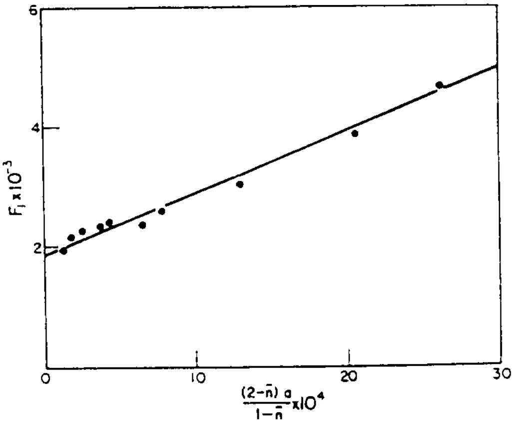

FIG. 4.—Rossotti and Rossotti's method. Computation of β_1 for zinc-TCA system, where $F_1 = \bar{n}/(1-\bar{n})a$.

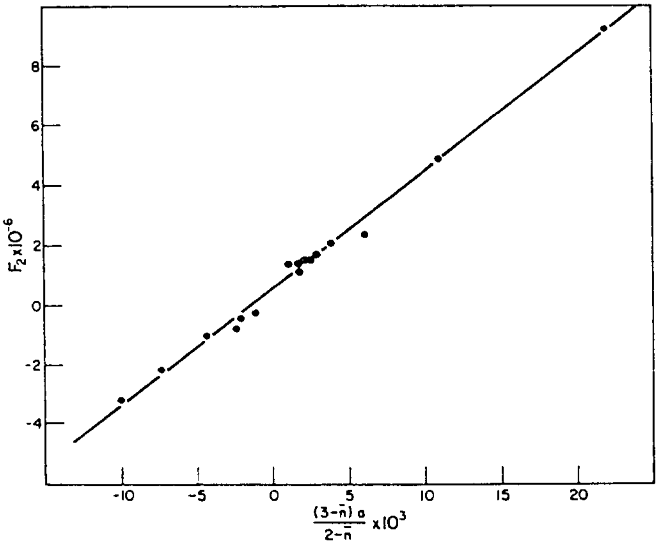

FIG. 5.—Rossotti and Rossotti's method. Computation of β_2 and β_3 for zinc-TCA system, where $F_2 = [\bar{n} - \beta_1(1-\bar{n})a]/(2-\bar{n})a^2$.

TABLE III.—DATA FOR ZINC-TCA COMPLEXES, OBTAINED FROM ONE POLAROGRAPHIC EXPERIMENT

B_{Zn}, M	$\Delta E_{1/2}$	log α_0	α_0	a, M	$\bar{n}_{Zn}$
$4 \cdot 80 \times 10^{-3}$	240·5	−8·45	$3 \cdot 55 \times 10^{-9}$	$1 \cdot 15 \times 10^{-2}$	3·44
$9 \cdot 60 \times 10^{-3}$	212·0	−7·54	$2 \cdot 88 \times 10^{-8}$	$4 \cdot 04 \times 10^{-3}$	2·50
$1 \cdot 20 \times 10^{-2}$	199·3	−7·02	$9 \cdot 55 \times 10^{-8}$	$2 \cdot 22 \times 10^{-3}$	2·15
$2 \cdot 28 \times 10^{-2}$	185·5	−6·54	$2 \cdot 88 \times 10^{-7}$	$1 \cdot 28 \times 10^{-3}$	1·17
$3 \cdot 12 \times 10^{-2}$	175·5	−6·20	$6 \cdot 30 \times 10^{-7}$	$8 \cdot 64 \times 10^{-4}$	0·87
$4 \cdot 20 \times 10^{-2}$	167·0	−5·91	$1 \cdot 23 \times 10^{-6}$	$6 \cdot 20 \times 10^{-4}$	0·65
$5 \cdot 28 \times 10^{-2}$	165·5	−5·85	$1 \cdot 41 \times 10^{-6}$	$5 \cdot 78 \times 10^{-4}$	0·52
$6 \cdot 48 \times 10^{-2}$	160·5	−5·68	$2 \cdot 08 \times 10^{-6}$	$4 \cdot 75 \times 10^{-4}$	0·43
$8 \cdot 68 \times 10^{-2}$	151·8	−5·38	$4 \cdot 16 \times 10^{-6}$	$3 \cdot 36 \times 10^{-4}$	0·33

Conditions: $B_{Pb} = 1 \cdot 10^{-3} M$ $Pb(NO_3)_2$; $A = 3 \cdot 10^{-2} M$ TCA; 0·05M formate buffer, pH = 4·00 ± 0·05; 0·008% gelatine; volume 25 ml; ionic strength $\mu = 0 \cdot 2$ (KNO_3); temperature 25 ± 0·2°C; titrated with 1·2M $Zn(NO_3)_2$.

First the dependence of the amalgam electrode potential on the concentration of zinc ions in the absence of complexing agents was studied. Experiments showed that over a wide range of zinc concentration a plot of E *vs.* $-\log\,[\mathrm{Zn}^{2+}]$ is linear, but conditions could not be found under which the slope had the theoretical value of 29·5 mV at 25°. The experimentally observed slope of 28 mV was used in the calculations [see equation (6)].

From the relationships[8]

$$(E)_A = E_0' - (RT/zF)\ln b \qquad \text{and} \qquad (E)_{A=0} = E_0' - (RT/zF)\ln B \tag{5}$$

we calculated

$$(\Delta E)_B = (E)_{A=0} - (E)_A = \frac{RT}{zF}\ln\frac{b}{B} = 0{\cdot}028\log\alpha_0. \tag{6}$$

From the potential of the amalgam electrode before and after the addition of the ligand, the relationship $\log\alpha_0$ *vs.* $\log A$ was found (see Table IV and Fig. 6 black circles). As the complexes formed were not particularly strong we could not use the approximation

TABLE IV.—DATA FOR ZINC–TCA COMPLEXES, OBTAINED FROM ONE POTENTIOMETRIC EXPERIMENT

A, M	$-\log A$	E, mV	ΔE, mV	$-\log\alpha_0$	$\bar{n}$	a, M
—	—	1065·7	—	—	—	—
$2{\cdot}24 \times 10^{-4}$	3·65	1066·7	1·3	0·047	0·10	$1{\cdot}04 \times 10^{-4}$
$8{\cdot}96 \times 10^{-4}$	3·05	1071·4	6·0	0·218	0·27	$5{\cdot}72 \times 10^{-4}$
$2{\cdot}24 \times 10^{-3}$	2·65	1080·7	15·3	0·556	0·93	$1{\cdot}12 \times 10^{-3}$
$3{\cdot}14 \times 10^{-3}$	2·50	1087·1	21·7	0·790	1·29	$1{\cdot}59 \times 10^{-3}$
$8{\cdot}96 \times 10^{-3}$	2·05	1121·2	55·8	2·03	2·50	$5{\cdot}96 \times 10^{-3}$
$2{\cdot}24 \times 10^{-2}$	1·65	1156·3	90·9	3·30	2·86	$1{\cdot}90 \times 10^{-2}$
$4{\cdot}48 \times 10^{-2}$	1·35	1180·8	115·1	4·20	2·86	$4{\cdot}14 \times 10^{-2}$

Conditions; $B = 1{\cdot}2 \times 10^{-3}M$ $\mathrm{Zn(NO_3)_2}$; 0·01M formate buffer, pH = 4·00 ± 0·05; volume 25 ml; ionic strength $\mu = 0{\cdot}1$ ($\mathrm{KNO_3}$); temperature 25 ± 0·2°C; titrated with 2M TCA.

$$\bar{n} \sim \frac{A}{B} \tag{7}$$

which is necessary for the graphical construction of the Fronaeus integral.

Approximate values of $\bar{n}$ were obtained graphically from the relationship

$$\frac{d\log\alpha_0}{d\log A} \sim -\bar{n}. \tag{8}$$

These values of $\bar{n}$ were then substituted into

$$a = A - \bar{n}B \tag{9}$$

to give preliminary values of a. By use of the method of successive approximations the correct relationship of $\log\alpha_0$ to $\log a$ was found (see Fig. 6—points ●).

Conditional constants were determined from the data $\alpha_0(a)$ by Leden's method.[8] The plots of the functions F_1 and F_2 against a, from which the values of β_1, β_2 and β_3 were obtained, are shown in Figs. 7 and 8.

Experiments performed with various total concentrations of the central ion established the mononuclearity of the system.

The stability constants of the cadmium–TCA complexes were determined analogously but the Fronaeus integral was used to obtain the free ligand concentration as described previously.[7] Some experimental results are shown in Table V.

The concentration stability constants were computed by multiplying the conditional constants by the value of the side-reaction coefficient α_H for TCA at pH = 4, calculated from the proton stability constants[5,7] $\log\beta_1^H = 3{\cdot}75$ and $\log\beta_2^H = 6{\cdot}67$ at 25°. The values of the concentration stability constants found are presented in Table VI, from which it can be seen that the results of the two methods show good agreement.

The errors of the values of the stability constants were calculated by taking into consideration the possible errors in the measured potentials of the dropping mercury electrode and the amalgam electrode. The latter were measured with a precision of ±1 mV. In the case of the polarographic study of zinc–TCA complexes the errors in the stability constants were found by taking into consideration

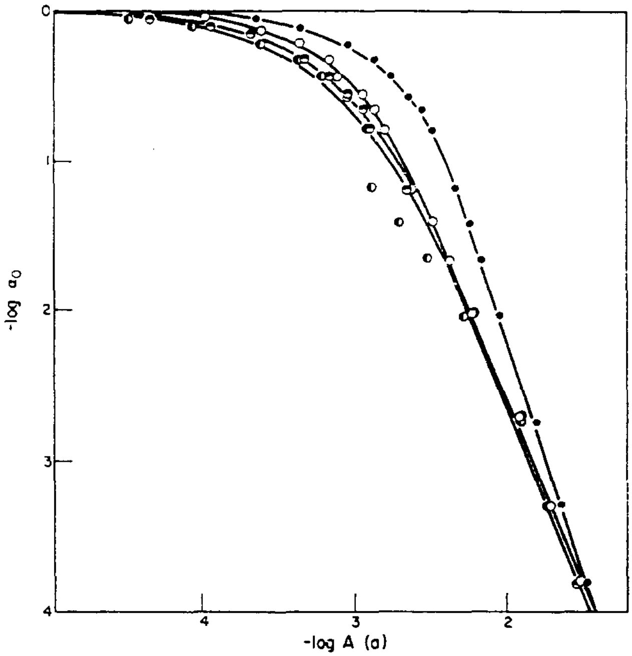

FIG. 6.—Dependence of log α_0 on log $A(a)$ for zinc-TCA system.

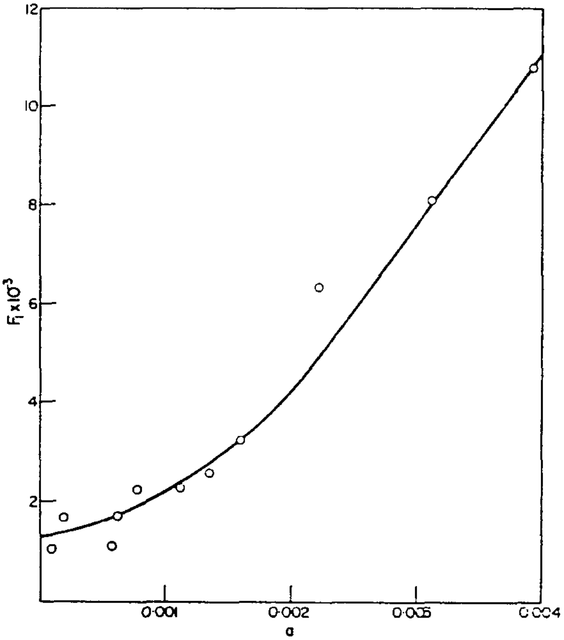

FIG. 7.—Leden's method. Computation of β_1 for zinc-TCA system, where $F_1 = (F_0 - 1)/a$ and $F_0 = 1/\alpha_0$.

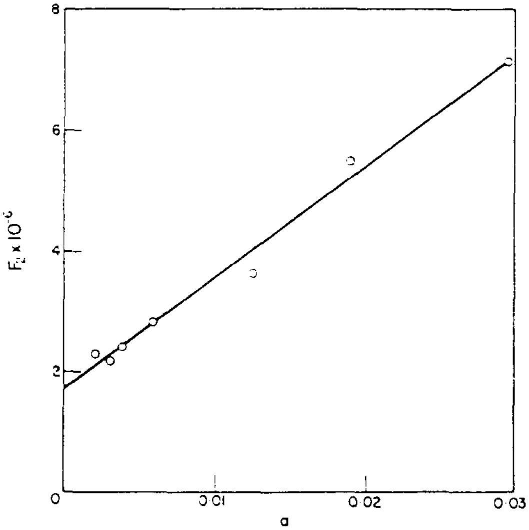

Fig. 8.—Leden's method. Computation of β_2 and β_3 for zinc–TCA system, where $F_2 = (F_1 - \beta_1)/a$.

Table V.—Data for cadmium–TCA complexes, obtained from one potentiometric experiment

A, M	E, mV	α_0	$\bar{n}$	a, M
—	665·0	—		
$6{\cdot}24 \times 10^{-5}$	674·9	$4{\cdot}60 \times 10^{-1}$	0·58	$4{\cdot}22 \times 10^{-6}$
$1{\cdot}25 \times 10^{-4}$	688·8	$1{\cdot}28 \times 10^{-1}$	1·07	$1{\cdot}75 \times 10^{-5}$
$3{\cdot}74 \times 10^{-4}$	746·3	$9{\cdot}11 \times 10^{-4}$	1·51	$2{\cdot}23 \times 10^{-4}$
$6{\cdot}24 \times 10^{-4}$	770·5	$1{\cdot}10 \times 10^{-4}$	1·76	$4{\cdot}48 \times 10^{-4}$
$1{\cdot}25 \times 10^{-3}$	795·4	$1{\cdot}32 \times 10^{-5}$	3·00	$9{\cdot}50 \times 10^{-4}$
$2{\cdot}18 \times 10^{-3}$	814·2	$2{\cdot}51 \times 10^{-6}$	3·00	$1{\cdot}88 \times 10^{-3}$
$4{\cdot}65 \times 10^{-3}$	842·1	$2{\cdot}29 \times 10^{-7}$	3·00	$4{\cdot}35 \times 10^{-3}$
$6{\cdot}24 \times 10^{-3}$	859·9	$5{\cdot}02 \times 10^{-8}$	3·00	$5{\cdot}94 \times 10^{-3}$

Conditions: $B = 1{\cdot}10^{-4}M$ Cd(NO$_3$)$_2$; 0·01M formate buffer, pH = 4·00 ± 0·05; volume 25 ml; ionic strength $\mu = 0{\cdot}1$ (KNO$_3$); temperature 25 ± 0·2°C; titrated with 0·2M TCA.

Table VI.—Values of the concentration stability constants

	Polarographic method	Potentiometric method
Pb	$\log \beta_2 = 13{\cdot}20 \pm 0{\cdot}15$	$\log \beta_1 = 7{\cdot}30 \pm 0{\cdot}10$* $\log \beta_2 = 13{\cdot}00 \pm 0{\cdot}20$*
Cd	$\log \beta_3 = 13{\cdot}60 \pm 0{\cdot}20$	$\log \beta_1 = 5{\cdot}4 \pm 0{\cdot}4$ $\log \beta_2 = 9{\cdot}3 \pm 0{\cdot}3$ $\log \beta_3 = 13{\cdot}7 \pm 0{\cdot}5$
Zn	$\log \beta_1 < 3{\cdot}8$ $\log \beta_2 = 6{\cdot}4 \pm 0{\cdot}4$ $\log \beta_3 = 9{\cdot}3 \pm 0{\cdot}2$	$\log \beta_1 = 3{\cdot}4 \pm 0{\cdot}3$ $\log \beta_2 = 6{\cdot}6 \pm 0{\cdot}2$ $\log \beta_3 = 8{\cdot}9 \pm 0{\cdot}3$

* Results from previous work.[7]

the errors in the experimental data for $\bar{n}$ and a. Both the values of stability constants and limits of error shown in Table VI are averaged from at least 7 separate experiments for each constant.

Zusammenfassung—Die Stabilitätskonstanten der Komplexe von Blei, Cadmium und Zink mit Dithiocarbaminoessigsäure (TCA) wurden bestimmt. Die Komplexe von Blei und Cadmium wurden polarographisch untersucht; für die Zink-TCA-Komplexe wurde eine polarographische Konkurrenzmethode verwendet. Die TCA-Komplexe von Zink und Cadmium wurden auch potentiometrisch mit einer Amalgamelektrode untersucht. Die Stabilitätskonstanten waren: Blei: $\log \beta_2 = 13{,}2$; Cadmium: $\log \beta_1 = 5{,}4$ (pot.), $\log \beta_2 = 9{,}3$ (pot.), $\log \beta_3 = 13{,}7$ (pot.), 13,6 (pot.); Zink: $\log \beta_1 = 3{,}4$ (pot.), $<3{,}8$ (pol.), $\log \beta_2 = 6{,}6$ (pot.), 6,4 (pol.), $\log \beta_3 = 8{,}9$ (pot), 9,3 (pol.).

Résumé—On a déterminé les constantes de stabilité des complexes du plomb, du cadmium et du zinc avec l'acide dithiocarbaminoacétique (TCA). On a étudié les complexes du plomb et du cadmium avec le TCA au moyen d'une méthode polarographique. On a utilisé une méthode polarographique concurrente pour l'étude des complexes zinc-TCA. Les complexes du zinc et du cadmium avec le TCA ont été aussi étudiés potentiométriquement avec une électrode à amalgame. Les constantes de stabilité trouvées sont: plomb, $\log \beta_2 = 13{,}2$; cadmium, $\log \beta_1 = 5{,}4$ (pot.), $\log \beta_2 = 9{,}3$ (pot.), $\log \beta_3 = 13{,}7$ (pot.), 13,6 (pol.); zinc, $\log \beta_1 = 3{,}4$ (pot.), $<3{,}8$ (pol.), $\log \beta_2 = 6{,}6$ (pot.), 6,4 (pol.) $\log \beta_3 = 8{,}9$ (pot.), 9,3 (pol.).

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EXTRACTION OF PROTACTINIUM FROM MINERAL ACID-ALCOHOL MEDIA

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Summary—The extraction of protactinium with organic solvents has been investigated in the presence of water-miscible alcohols and acetone. These additives were found to increase considerably the extraction of protactinium in the cases of trilaurylamine, tributyl phosphate and isobutyl methyl ketone. The influence was less in the case of thenoyltrifluoroacetone. In mixtures of an acid with various alcohols, the influence depended on the alcohol concentration, the acidity and on the chain lengths and dielectric constants of the alcohol introduced into the extraction system.

DURING previous work[1,2] it was observed that the presence of various amounts of water-miscible alcohols or ketones in the aqueous phase greatly influences the extraction of elements with a tertiary amine (tridodecylamine) and an organophosphorus solvent (tributyl phosphate). The influence of such organic additives on extraction has been attributed to two different effects. Thus the decrease in hydration in the aqueous phase, as the mole fraction of water decreases, results in an increase in the formation of extractable (negatively charged or neutral) metal complexes. This leads to an extraction increase. On the other hand the decrease of the amount of water in the aqueous phase results in a parallel increase of the effective acid concentration. This sometimes leads to a decrease of extraction, owing to the competition between the extractable metal species and the acid for the available molecules of the extracting agent.

Although the addition of water-miscible alcohols or ketones complicates the extraction systems from the theoretical point of view, very useful applications of such systems in chemical and radiochemical separations can be achieved. Thus the separation of silver and mercury and also silver and selenium, which could not be realized from pure mineral acid solutions, was found to be easy when mixed media were used.[2]

In the present work, the extraction of protactinium and its separation from solutions of mineral acids with solutions of organic solvents in non-polar diluents has been investigated in the absence and presence of miscible organic additives. Work on protactinium is particularly interesting because of its production in reactors working on thorium-232 and also because of its complicated aqueous chemistry. Thus protactinium exists in the form of various hydroxo- rather than simple metallic or oxo-complexes in hydrochloric and nitric acid solutions.[3,4]

Protactinium extraction from pure aqueous acidic solutions with organic solvents has been a subject of extensive studies by many workers. Such studies have been summarized in a number of articles[4–9] and useful separation methods for protactinium in various acidic media have been developed.[5–12]

EXPERIMENTAL

Reagents

Solvents. Pure tridodecylamine or trilaurylamine (TLA),[11] tri-n-butyl phosphate (TBP), isobutyl methyl ketone (IBMK) and thenoyltrifluoroacetone (TTA) were used in the present work without further purification.

Diluents. The non-polar diluents employed (xylene, benzene and chloroform) were reagent grade quality.

Organic additives. The aliphatic alcohols used (methanol, ethanol, n-propanol, isopropanol and isobutanol) and acetone were also reagent-grade solvents.

Tracer stock solutions. The isotope ^{233}Pa was prepared from irradiated thorium nitrate, which was dissolved in 6*M* hydrochloric acid. This isotope was selectively separated from the target solution by extraction with 20% trioctylamine solution in xylene and stripping from the organic phase with 1·5*M* hydrochloric acid. The strip solution was then mixed with an equal amount of concentrated hydrochloric, nitric or hydrobromic acid for use in studies with the respective acids. The isotope ^{234}Th was prepared from uranyl nitrate (50 g) solution in 6*M* hydrochloric acid (100 ml) by successive extraction of uranium with 30% TBP solution in xylene; ^{234}Th remained in the aqueous phase. The isotope solution was evaporated to a small volume (2–5 ml) and subsequently mixed with 10 ml of 8*M* nitric acid or 10 ml of 6*M* hydrochloric acid. Other tracers were available in this laboratory from previous studies.[3]

Apparatus

The purity of all isotopes was checked by γ-ray spectrometry with a Nuclear-Chicago, single-channel analyser (type 132 B) connected to a 3 × 3 in. NaI(Tl) crystal. An ECKO scintillation counter connected to a well-type 2·5 × 2·5 in. NaI(Tl) crystal and a photomultiplier tube was employed for measuring the radioactivity in the case of all isotopes except ^{234}Th. The activity of the latter was measured with a Phillips β-counter connected to a thin end-window G–M tube.

Extraction procedure

The solutions of solvents in diluents and the mixtures of acids and water-miscible alcohols (or acetone) were made by volume. Extraction experiments were performed in graduated tubes by shaking (on a mechanical shaker) equal volumes (usually 5 ml) of the two phases at a constant temperature, 25 ± 0·1°, for 40 min. After centrifugation, aliquots of both phases were counted in the γ-scintillation counter (or the β-counter, after evaporation to dryness on glass trays in the case of ^{234}Th). Measurements of the radio-activity were conducted under standard conditions. Care was taken to check the activity balance and losses were kept below 2%. The distribution ratio (*E*) was calculated as the ratio of the activity in the organic to that in the aqueous phase. All experiments were carried out only in duplicate, owing to the high reproducibility of results.

RESULTS AND DISCUSSION

Mutual solubility and swelling of the organic phase

In the present work, detailed study on mutual solubility of the various components and on the swelling of the organic phase has not been made. Generally, however, it has been found that at concentrations of alcohol of about 30% and less in the aqueous phase, the change in volumes of phases is of the same order as in the case of pure aqueous mineral acid solutions. At higher alcohol concentrations the swelling of the organic phase is only noticeable with long chain alcohols (propanol and butanol). In other words swelling increases with increasing chain length and dielectric constant of the alcohol (see Table I).

Swelling also increases with the amount of alcohol added. Further, in the case of IBMK (undiluted) and TBP (50%) swelling is greater than in the case of TLA(0·3*M*) or TTA(0·5*M*). This implies that swelling is also dependent on the solvent used. Sometimes only one phase is formed when the concentration of alcohol is increased

TABLE I.—DIELECTRIC CONSTANTS (at 25°C) OF THE LIQUIDS STUDIED

Liquid	Dielectric constant
Water	78·54
Methanol	32·63
Ethanol	24·3
n-Propanol	20·1
isoPropanol	18·3
isoButanol	17·7
Acetone	20·7
Benzene	2·274
p-Xylene*	2·270
Chloroform*	4·806

* At 20°C

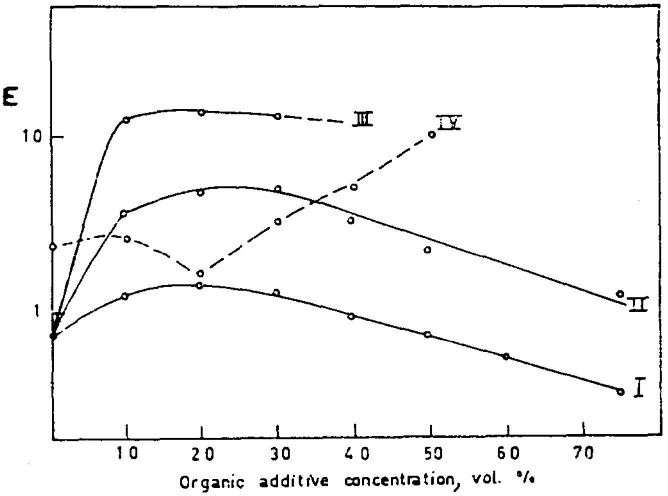


FIG. 1.—Effect of organic additives on E for extraction of Pa with 0·3M TLA in xylene from 3·9M HNO_3.
I—Methanol; II—ethanol; III—isopropanol; IV—corresponding data for Th in ethanol–HNO_3 mixtures.

above a certain limit. The concentration of alcohol above which one phase is formed decreases with increase of the chain length of the alcohol. This is clear in the case of extraction with 0·3M TLA, where one phase is formed for mixtures of concentrated hydrochloric acid and alcohol containing $> 90\%$ methanol or $> 85\%$ isopropanol.

Because in systems involving mixed media the aqueous phase also contains organic matter, we can use the terms "non-polar" phase (the phase containing the solvent) and "polar" phase.

Extraction of protactinium with TLA

In Fig. 1 are given data on the extraction of protactinium with 0·3M TLA from 3·9M nitric acid in the presence of varying amounts of methanol, ethanol and isopropanol in the aqueous phase. These data show that with the increase of alcohol concentration the extraction of protactinium increases, passes through a maximum and then decreases. The influence of alcohol increases with the increase of the chain

TABLE II.—EFFECT OF ETHANOL AND ISOPROPANOL ON *E* FOR Pa AND SOME OTHER ELEMENTS
(Aqueous phase: 3·9*M* HNO_3: organic phase: 0·3*M* TLA.)

Ion	*E*		
	no alcohol	50% ethanol	10% isopropanol
Protactinium	0·65	2·5	12·5
Thorium	0·35	10	2·5
Silver	0·03	0·08	0·02
Mercury(II)	1·0	3·0	2·5
Selenium(IV)	0·025	0·07	0·02
Cobalt	<0·001	<0·001	<0·001
Zinc	0·015	0·15	0·01
Iron(III)	<0·010	0·1	1·12

length of the alcohol. Thus the value of *E* increases from 0·7 in pure aqueous 3·9*M* nitric acid to >10 when 10% isopropanol solution and the same nitric acid concentration are employed. The presence of maxima in the partition curves confirms the suggestion of two opposing effects.

Curve III (Fig. 1) has been completed as a dotted line above 30% isopropanol, because of the considerable swelling of the organic phase. Higher concentrations of isopropanol are fortunately unnecessary, since they do not give any further increase of protactinium extraction.

Data on the extraction of protactinium and some other elements from 3·9*M* nitric acid in pure aqueous solutions, 50% ethanol and 10% isopropanol are presented in Table II.

The data above show that although the extraction of protactinium, thorium, mercury and iron increases considerably in the presence of water-miscible alcohols the extraction of other elements remains almost unchanged. For determining the best separation conditions for these elements in nitric·acid–alcohol mixtures, their extraction in the presence of various amounts of the alcohols should be studied in more detail. It is clear, however, that the separation of protactinium, thorium and mercury from selenium, silver, cobalt and zinc in the presence of 10% of isopropanol is much more effective than from pure aqueous solutions. The separation of iron from the same four elements is also only possible in the presence of 10% of isopropanol.

Figure 2 shows the results of varying amounts of alcohols and acetone on the value of *E* for protactinium extraction from 2·8*M* hydrochloric acid by 0·3*M* TLA in xylene. From the curves it is seen that protactinium extraction considerably increases with the alcohol (or acetone) concentration in the aqueous solution. The increase is more marked at lower alcohol concentrations. This can be explained by the contribution of the second effect (reaction of the amine monochloride to give the amine dichloride, $TLAH^+.HCl_2^-$), at higher hydrochloric acid molarities. In general, the influence of organic additives increases in the order methanol < acetone < ethanol < isopropanol, although the regularity is interrupted at lower concentrations of acetone in the mixtures. The value of *E* increases from about 0·1 in pure aqueous 2·8*M* hydrochloric acid to about 10 in 20% isopropanol, 65% ethanol or 70% acetone solutions of the same hydrochloric acid molarity.

To show the effect of the chain length and dielectric constant (DC) of alcohols on

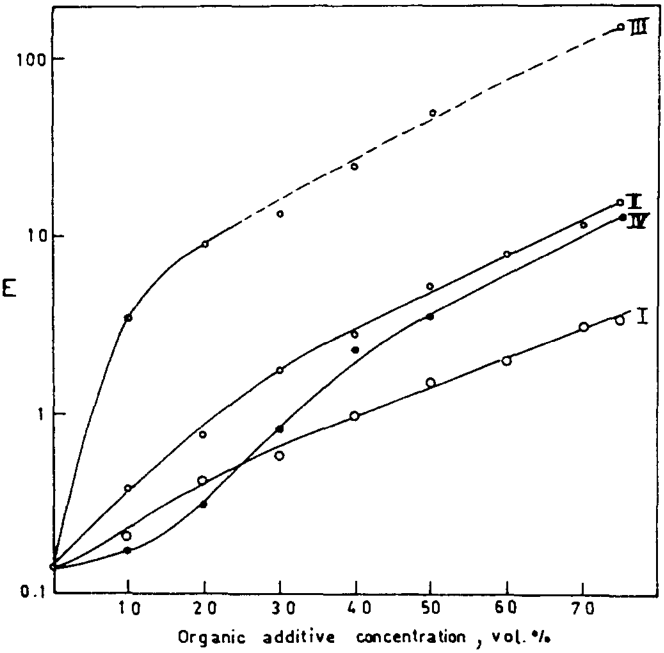


FIG. 2.—Effect of organic additives on E for extraction of Pa with 0·3M TLA in xylene from 2·9M HCl.
I—Methanol; II—ethanol; III—isopropanol; IV—acetone.

the extraction of protactinium with TLA, the values of E were plotted against the number of carbon atoms (Fig. 3) and 1/DC (Fig. 4) for the pure alcohols introduced into the system. For every curve the overall acidity and alcohol concentration were kept constant. It is clear that extraction increases with the increase of chain length and dielectric constant of the alcohols. The effect is less marked at lower alcohol concentration, which could be the result of the common effect of higher water content in the mixtures.

The effect of water-miscible alcohols on protactinium extraction has also been investigated at increasing hydrochloric acid molarities in the aqueous phase (Figs. 5 and 6). It is again evident that at the same acidity, extraction is much greater in the presence of alcohols in the aqueous phase, although the trends of the curves are similar. In other words, in any mixture containing any alcohol, extraction is higher than if this alcohol is replaced by water. In the case of mixtures of methanol and concentrated hydrochloric acid (Fig. 6), the presence of a high concentration of alcohol in the aqueous phase results in the decrease of the specific gravity of the latter and the position of the phases is reversed for 5% of concentrated hydrochloric acid and 95% of methanol. At 10% acid and 90% methanol the separation of phases is difficult, although after centrifugation, the upper phase was found to be the solvent layer. It is to be expected that there would be a concentration of acid, between 5 and 10% in methanol, for which the separation of phases is not possible owing to the equality of the densities of the polar and non-polar phases. The replacement of xylene by benzene for diluting the TLA made little difference (Table III).

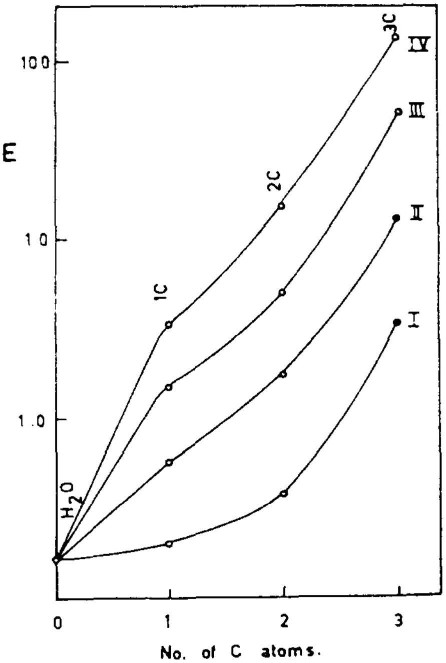


FIG. 3.—Effect of chain length of alcohols on *E* for extraction of Pa from 2·9*M* HCl.

I—10% alcohol; II—20% alcohol; III—50% alcohol; IV—70% alcohol.

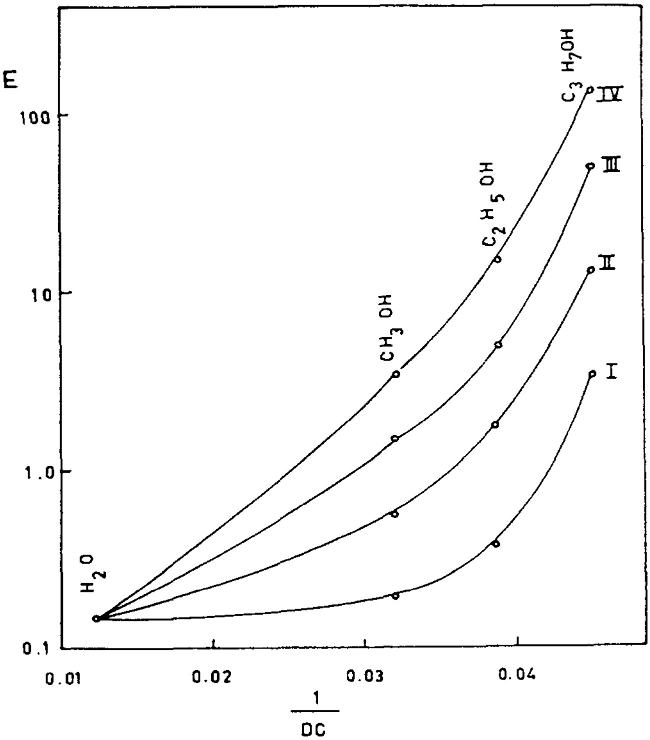


FIG. 4.—Effect of dielectric constant of alcohols on *E* for extraction of Pa from 2·9*M* HCl.

I—10% alcohol; II—20% alcohol; III—50% alcohol; IV—70% alcohol.

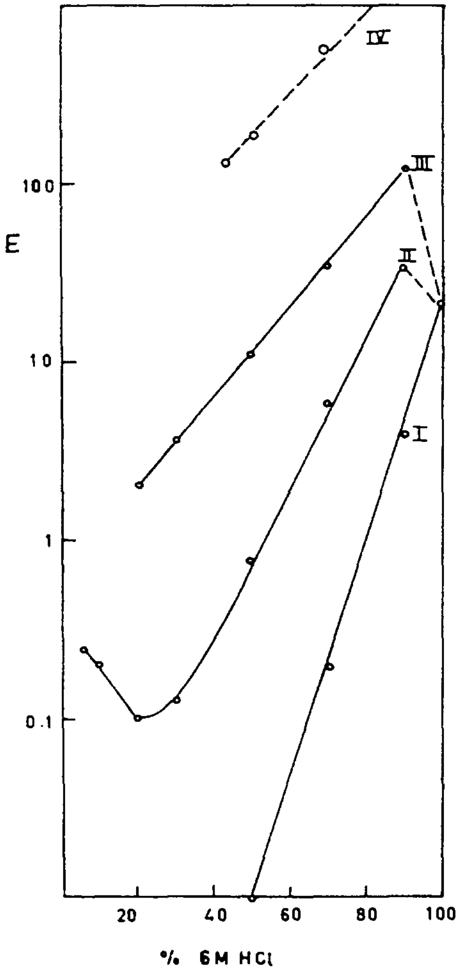


FIG. 5.—Effect of 6*M* HCl content on the extraction of Pa with 0·3*M* TLA in xylene. I—Water; II—methanol; III—ethanol; IV—isopropanol.

It was also interesting to study the effect of alcohols on the extraction of protactinium with solutions of TLA in chloroform, a diluent which is heavier than water. The addition of alcohols in this case increases the difference of the specific gravities of organic (heavier) and aqueous phases, and thus favours rapid phase separation. Figure 7 shows the experimental results for extraction by 0·3*M* TLA from mixtures of methanol and hydrochloric acid and mixtures of methanol and nitric acid. In the case of chloride extraction the values of *E* considerably increase with the increase of methanol concentration over the range of acidity studied. On the other hand nitrate extraction is only slightly affected by the presence of up to 75% of methanol. It is expected, however, that a greater increase in nitrate extraction would be achieved by using longer chain alcohols (see Fig. 1).

Data on the extraction of protactinium and some other elements from 2·9*M* hydrochloric acid in pure aqueous solutions and in 20% isopropanol mixtures are given in Table IV.

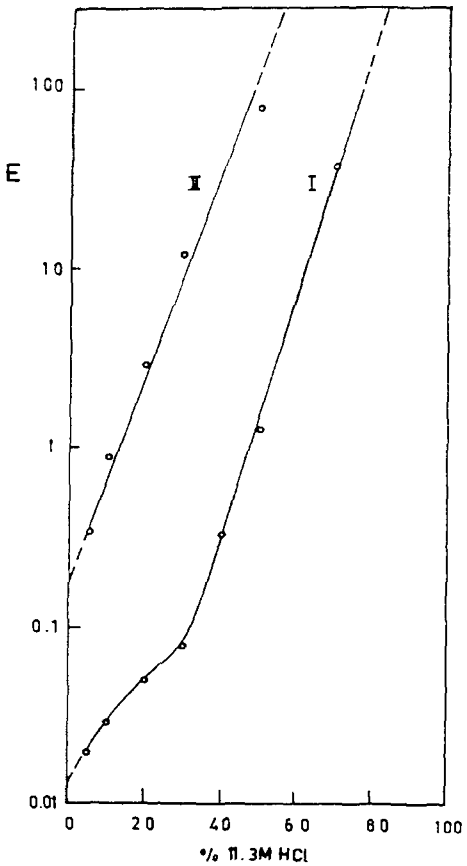


FIG. 6.—Effect of concentrated hydrochloric acid content on *E* of Pa extraction with 0·3*M* TLA.
I—Water; II—methanol.

TABLE III.—EXTRACTION OF Pa FROM 2·9 AND 6*M* HYDROCHLORIC ACID BY 20% TLA

[HCl], *M*	[Methanol], %	*E*	
		xylene	benzene
2·9	0	0·16	0·13
	10	0·18	0·15
	20	0·43	0·54
	30	0·58	0·61
	40	1·0	0·79
	50	1·5	1·6
6·0	0	6·3	11·4
	10	27·0	30·6
	20	30·2	31·3
	30	56·8	61·7
	40	>100	96·0
	50	85	80·0

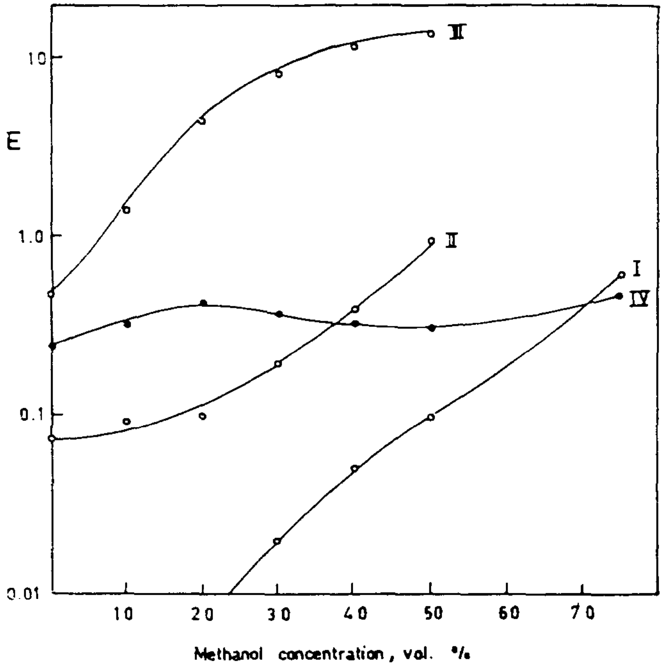


FIG. 7.—Effect of organic additives on *E* for extraction of Pa with 0·3*M* TLA in chloroform from methanol–acid mixtures.
I—2·9*M* HCl; II—4·3*M* HCl; III—5·75*M* HCl; IV—3·9*M* HNO_3.

TABLE IV.—EFFECT OF ISOPROPANOL ON *E*
(Extraction with 0·06*M* TLA in xylene from 2·9*M* HCl)

Ion	*E*	
	pure aqueous	20% isopropanol
Protactinium	0·9	2·8(8)*
Thorium	0·001	0·02
Silver	2·0	0·40(5·0)
Mercury(II)	34·0	13·2(50·0)
Selenium(IV)	0·15	0·14(0·35)
Cobalt	0·02	0·006(0·1)
Zinc	80·0	6·0(160)
Iron	4·5	2·2(10·0)

* In brackets are given the values of *E* for extraction with 0·3*M* TLA in xylene.

The data above show that protactinium and silver, which cannot be separated from each other in pure aqueous solutions, are easily separable in mixed media. This can be achieved by one extraction step followed by three scrubbing steps. The reason for the decrease of extraction of silver, mercury and zinc in the presence of alcohols has been discussed previously.[2] The higher extraction of protactinium in the presence of alcohols can also be utilized for its separation from selenium and cobalt, the extraction of which is only slightly affected by the presence of alcohols. Extracted protactinium can always be stripped from the organic phase by 1·5*M* hydrochloric acid.[12]

TABLE V.—EXTRACTION OF Pa WITH 50% TBP IN XYLENE FROM 5·8*M* HCl

[HCl], *M*	[Methanol], vol.%	Volume of* org. phase, *ml*	Volume* of aq. phase, *ml*	*E*
1·73	—	—	—	0·01
	70	2·4	1·6	0·16
2·3	—			0·06
	80	2·7	1·3	2·12
2·88	—			0·07
	50	2·25	1·75	0·28
3·45	—			0·5
	70	2·3	1·7	9·0
4·03	—			0·2
	30	2·2	1·8	1·09
5·75	—			6·2
	50	2·25	1·75	4·3
8·05	—			12·5
	30	2·15	1·85	70

* In the case of pure aqueous solutions the volume of the organic phase is 2·10–2·15 ml and that of the aqueous phase is 1·85–1·90 ml, depending on the acidity. The volume of each phase before extraction is 2·0 ml.

TABLE VI.—EFFECT OF ALCOHOLS ON THE EXTRACTION OF Pa FROM 5·1*M* HBr BY 50% TBP

Aqueous phase	*E*
pure aqueous	1·1
20% methanol	1·2
20% ethanol	7·0
20% n-propanol	3·2
20% isopropanol	11·0
20% isobutanol*	5·2

* Alcohol passes preferentially to the organic phase, the volume of which increases by about 20%.

Extraction of protactinium with TBP and IBMK

The effect of methanol concentration on the extraction of protactinium, with 50% TBP in xylene is illustrated in Table V. The data presented show that at a variety of acidities and methanol concentrations in the aqueous phase, protactinium extraction is always greater in the presence of alcohol. It is also interesting to study the extraction behaviour of uranium and thorium in such a system, since the separation of protactinium and these two elements from each other is important in modern reactor technology. The separation of the three elements by extraction with TBP from pure aqueous hydrochloric acid has already been reported in the literature.[14]

Above ~80% methanol only one phase is produced, which is possibly due to mutual solubility of the components in both phases.

The extraction of protactinium by 50% TBP from 5·1*M* hydrobromic acid in the absence and presence of 20% alcohol has also been studied. Results are given in Table VI.

Data on the extraction of protactinium with IBMK from 5·75*M* hydrochloric acid are presented in Table VII.

TABLE VII.—EXTRACTION OF Pa WITH IBMK FROM 5·75M HCl*

Methanol, %	Volume of organic phase, *ml*	Volume of aqueous phase, *ml*	E
0	10·1	9·9	1·01
10	10·25	9·75	4·03
20	10·5	9·50	10·1
30	11·4	8·50	15·9
40	12·6	7·40	21·4

* Original volume of each phase is 10 ml.

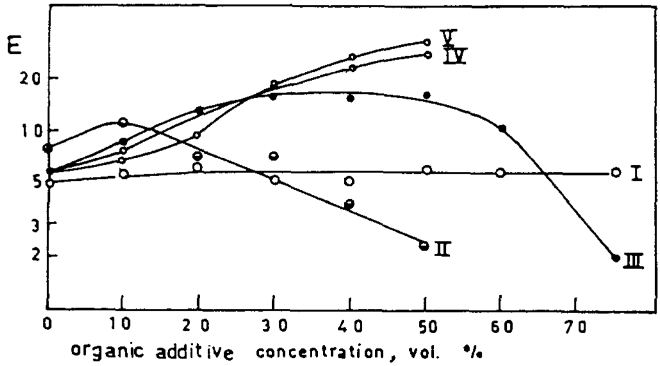


FIG. 8.—Effect of organic additives on E for extraction of Pa with 0·5M TTA in xylene. I—Methanol in 2M HCl; II—methanol in 5·75M HCl; III—methanol in 2M HNO_3; IV—ethanol in 2M HNO_3; V—isopropanol in 2M HNO_3.

These results show that protactinium extraction rises steeply with increase in methanol concentration. Thus the value of E increases 10-fold when 20% methanol is used instead of pure aqueous 5·8M hydrochloric acid, while the swelling of the organic phase is unimportant.

Extraction of protactinium with TTA

Results on the extraction of protactinium with TTA from nitric and hydrochloric acid solutions in the presence of alcohols are shown in Fig. 8. It is seen that the influence of alcohols is much less than in the case of extraction with TLA, TBP and IBMK. This is readily understood, since extraction with TTA, which is a chelating agent, is not affected by hydration in the aqueous phase. At 20–30% alcohol the influence of methanol, ethanol and isopropanol on the extraction of protactinium from 2M nitric acid is almost the same. At lower alcohol content the influence decreases in the order methanol > ethanol > isopropanol and at higher alcohol content, the influence is reversed.

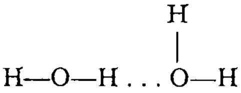
CONCLUSIONS

The addition of water-miscible alcohols has been known for some time to influence precipitation and ion-exchange chromatography.[15] The present work shows that the nature of solvent extraction from solutions of mineral acids in mixed media appears to be much more complicated than solvent extraction from pure aqueous solutions. Theoretical interpretation is more difficult because of insufficient data on the properties of electrolytes in mixed media. The influence of miscible organic additives can be related to a number of mutually related factors. Thus, these additives may influence complex formation, solvation and ionic and molecular interaction in the aqueous phase. Partition of water-miscible additives between organic and aqueous phases may also influence complex formation in the organic phase.

A relationship was demonstrated between the uptake of alcohol into the organic phase and polarity of this alcohol. For a mixture of water with an organic additive (with lower dielectric constant) in contact with a solution of a solvent in a non-polar diluent, it is expected that the uptake in the organic phase in the case of the organic additive would be greater than in the case of water. The selective uptake of organic additives increases with their concentration in the mixture, so a single phase may ultimately be formed.

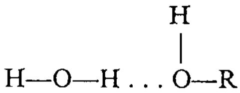
The substitution of increasing amounts of water by organic additives leads to a gradual dehydration of the hydrated metal ions in the aqueous phase.[16] This results in a parallel increase of ionic interaction, and hence of association in mixed media. Thus it has been reported that the stability of the negatively charged chloro-complexes in solution can be markedly increased by the introduction of such organic additives.[17–24] This must result in an increase in extraction of the ion-asociation (TBP extraction) or anion-exchange (TLA extraction) type. This can also be explained by the fact that dissociation of electrolytes decreases in the presence of organic additives with lower dielectric constants. This should bring about an increase in the degree of extraction of the types mentioned.

The loose combination, or intermolecular association, sometimes referred to as the formation of a "molecular compound" through a hydrogen bond is known to occur between two or more water molecules, a water molecule and a molecule of any other hydroxylic compound, or two molecules of the latter.[25] Thus a mixture of water and alcohol probably contains compounds such as:



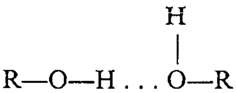
$$H{-}O{-}H\ldots\overset{H}{\overset{|}{O}}{-}H$$

(I)



$$H{-}O{-}H\ldots\overset{H}{\overset{|}{O}}{-}R$$

(II)



$$R{-}O{-}H\ldots\overset{H}{\overset{|}{O}}{-}R$$

(III)

and a mixture of water and a ketone contains beside compound (I), the compound $H{-}O{-}H\ldots OCR_2$ (IV). The tendency of formation and comparative stability of complexes I, II, III and IV must have also a certain effect on ion-association in the mixed aqueous phase and hence on the extraction.

Several other factors which also influence extraction, such as the ionic radii, ionic charge and ionic strength, all of which are being changed in the presence of organic additives, should also be taken into consideration.[26]

Acknowledgement—The authors are grateful to Dr. M. H. Etman for his valuable assistance.

Zusammenfassung—Die Extraktion von Protactinium mit organischen Lösungsmitteln wurde in Gegenwart von mit Wasser mischbaren Alkoholen und Aceton untersucht. Es wurde gefunden, daß diese Zusätze die Extraktion von Protactinium mit Trilaurylamin, Tributylphosphat und Isobutylmethylketon beträchtlich verbessern. Bei Thenoyltrifluoraceton war der Effekt geringer. Bei Gemischen einer Säure mit mehreren Alkoholen hind der Effekt von der Alkoholkonzentration, der Acidität sowie der Kettenlänge und der Dielektrizitätskonstanten des dem Extraktionssystem zugesetzten Alkohols ab.

Résumé—On a étudié l'extraction du protactinium par des solvants organiques en la présence d'alcools miscibles à l'eau et d'acétone. On a trouvé que ces additifs accroissent considérablement l'extraction du protactinium dans les cas de la trilaurylamine, du tributyl phosphate et de l'isobutyl méthylcétone. L'influence est moindre dans le cas de la thénoyltrifluoracétone. Dans des mélanges d'un acide avec divers alcools, l'influence dépend de la concentration de l'alcool, de l'acidité, et des longeurs de chaîne et des constantes diélectriques de l'alcool introduit dans le système d'extraction.

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THERMOANALYTICAL PROPERTIES OF ANALYTICAL GRADE REAGENTS—V. SODIUM HALATES*

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Summary—The thermoanalytical properties of sodium halates have been investigated by means of a derivatograph and a visual DTA instrument. The thermal decomposition of the compounds studied was found to proceed only in the melt phase to a measurable extent, while the corresponding sodium halides were being formed. For sodium chlorate the formation and decomposition of sodium perchlorate could also be observed. The comparison of the results of thermal investigations with results of X-ray measurements has shown that the ionic character of the chemical bonds is highest for sodium iodate and lowest for sodium chlorate.

IN the present paper we report, as in previous communications,[1-4] on the thermoanalytical properties of some sodium salts.

EXPERIMENTAL

Analytical grade sodium chlorate, sodium bromate and sodium iodate were investigated by means of a derivatograph 5 and a differential thermal analyser (DTA) equipped with a sensitive recorder constructed in our laboratories. The furnace was modified as shown in Fig. 1, so that the sample

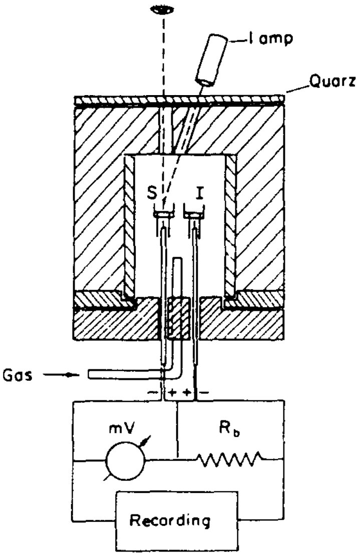

FIG. 1.—Modified furnace for visual inspection of sample during heating.

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* Part IV—*Talanta*, 1966, **13**, 67.

could be observed by an optical device during the measurements. The observing holes were covered with quartz plates to prevent heat loss and draught. This modification of the furnace did not cause any change in the DTA base line, as proved by calibration.

For the programmed heating of the apparatus an electronic linear temperature programming device was used which ensured control within ±0·3°.

The temperature and DTA signals were recorded by a two-channel Kipp–Zohnen BD2 type Micrograph.

Samples of 170–200 mg in weight were ground and sieved with a 350-mesh sieve. Samples of 10–50 mg in weight were used in the DTA instrument. The heating rate was 10°/min.

The reagents used were made available by E. Merck (Darmstadt, German Federal Republic) for which we would like to express our thanks.

RESULTS AND DISCUSSION

The thermal decomposition of sodium halates proceeds according to the general equation

$$2NaXO_3 \xrightarrow{\text{heat}} 2NaX + 3O_2.$$

where X is a halogen atom.

Sodium chlorate

Figure 2 shows the derivatogram of sodium chlorate. The endothermic peak at 260° on the DTA curve shows the melting of the sample, this temperature being in good agreement with the literature value.[6] Decomposition, an exothermic process, starts at 350°, and oxygen is evolved at a maximum rate at 480 and 550°. The endothermic peak at 790° on the DTA curve indicates the melting point of the sodium chloride

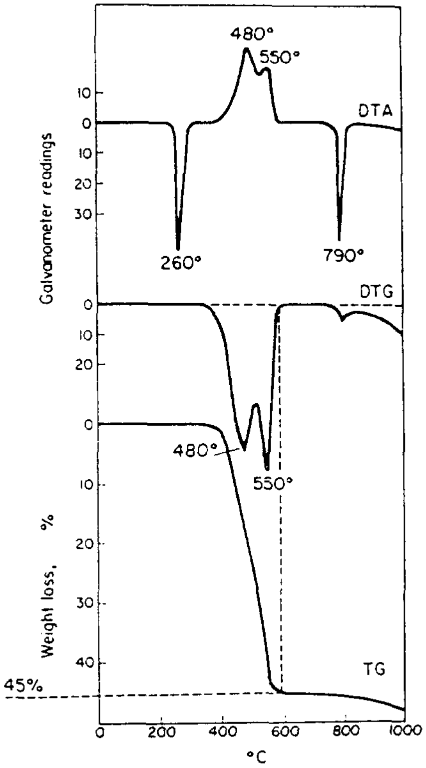

FIG. 2.—Derivatogram of sodium chlorate.

formed. If the starting material is pulverized sodium chlorate, the weight loss calculated from the TG curve is 5–8 % lower than the theoretical value, because the substance partly decomposes during pulverization. Figure 2 shows the derivatogram of the non-pulverized sample.

The double DTG and DTA peaks cannot be interpreted in terms of the general reaction equation given above. It may be assumed that sodium chloride formed during the decomposition hinders the departure of oxygen from the melt. The sodium chloride formed is dissolved in the sodium chlorate melt, so that the viscosity of the melt is increased and the rate of weight change reduced. As decomposition continues, sodium chloride is precipitated.

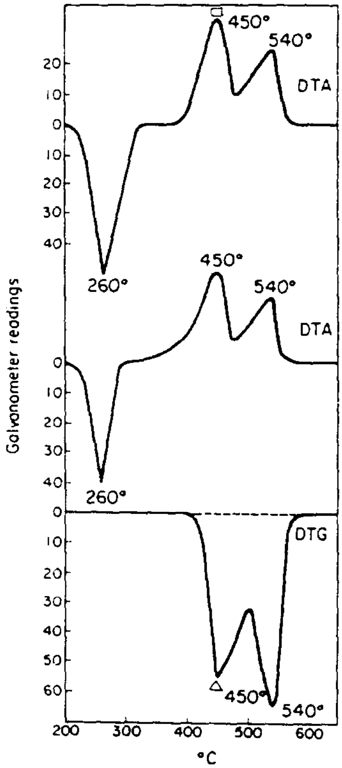

FIG. 3.—DTG and DTA curves for sodium chlorate.

Figure 3 shows the curves taken by the derivatograph (DTA and DTG), and by the DTA instrument. At the moment of solidifying, occurring at a temperature indicated by □ in the figure, the direction of the DTA curve changes suddenly and the rate of weight change begins to decrease (Δ). The heating rate was 5°/min.

As evidenced by literature data,[7–10] perchlorate is also formed during the decomposition of chlorates:

$$2NaClO_3 = NaClO_4 + NaCl + O_2.$$

Under the conditions of the present experiments sodium perchlorate is formed during the thermal decomposition of sodium chlorate, and decomposes at higher temperatures, oxygen and sodium chloride being formed. The maximum at 480° on the DTA curve may therefore be regarded as characteristic of the decomposition of sodium chlorate, and the peak at 550° to indicate the maximum rate of oxygen evolution from sodium perchlorate formed from sodium chlorate.

A series of experiments was carried out to prove these hypotheses. Derivatographic measurements were made with sodium chlorate samples to which sodium perchlorate was added in increasing amounts. Figure 4 shows the DTA and DTG curves of 1 : 1 mixture of sodium chlorate and perchlorate, and of the pure salts.

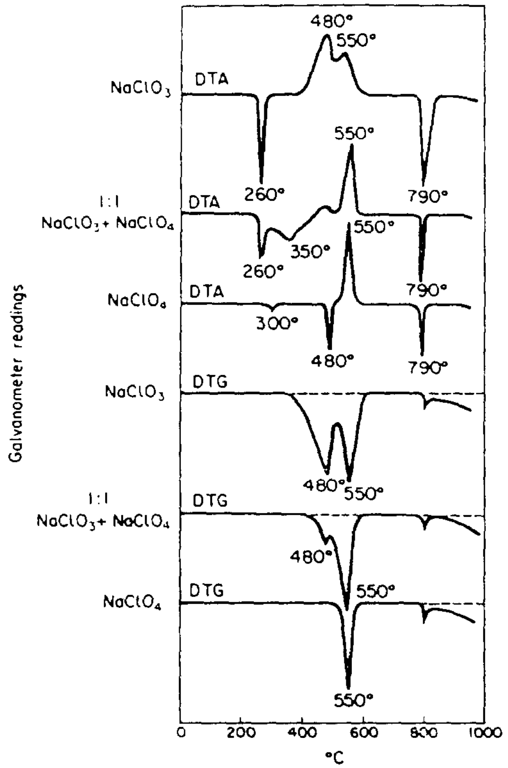

FIG. 4.—DTG and DTA curves for sodium perchlorate, sodium chlorate and a mixture of both.

The exothermic peak at 550° on the DTA curve of the mixture, and the corresponding DTG maximum, were found to be bigger than those in the curves for pure sodium chlorate. The increase in the height of the exothermic peak at 550° on the DTA curve, characteristic of the decomposition of pure sodium perchlorate is a proof of the formation of sodium perchlorate.

As shown by the measurements, the general reaction equation for the thermal decomposition of sodium halates gives the products of reaction correctly, but gives no information on the possible intermediate reaction stages.

The peaks at 550° on the DTG and DTA curves indicate partly the solidifying of sodium chloride produced during the decomposition and partly the thermal decomposition of sodium perchlorate.

Sodium bromate

The derivatogram of sodium bromate is presented in Fig. 5. The endothermic peak at 380° on the DTA curve indicates the melting of the substance (in good agreement with the literature value 11). The decomposition of the sample starts at the melting point. The exothermic peak at 400° on the DTA curve, and the corresponding DTG maximum, show the temperature where enthalpy and weight changes proceed at maximum rate. Decomposition is complete at 430° and sodium bromide remains in stoichiometric amounts. It has been assumed by Jack[12] on the basis of kinetic measurements that sodium bromate forms a eutectic with sodium bromide, but we could not prove this by measurements made under dynamic conditions.

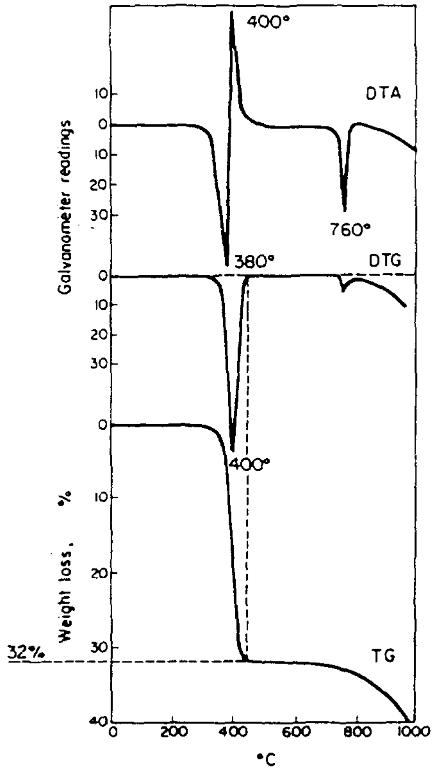

FIG. 5.—Derivatogram of sodium bromate.

It was observed in the DTA experiments that oxygen is evolved from the sample simultaneously with the rounding off of particles, and solid sodium bromide is precipitated during the decomposition.

The endothermic peak at 760° on the DTA curve indicates the melting of sodium bromide.

Sodium iodate

Figure 6 shows the derivatogram of sodium iodate. The endothermic peak at 420° on the DTA curve indicates the melting of sodium iodate. The melting point was found to be sharp, and no weight loss was observed above this temperature.

In the literature[13–15] the decomposition point is quoted rather than the melting point and it is stated that the melting of the substance is accompanied by decomposition. According to our derivatogram decomposition does not start below 500°. The endothermic peak at 620° on the DTA curve indicates the enthalpy change, and the peak at 610° on the DTG curve the temperature at which the rate of decomposition is maximum. Sodium iodide formed during the decomposition sublimed above 650°.

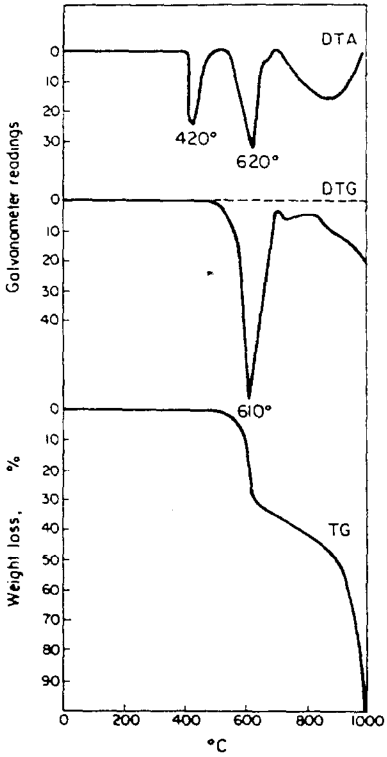

FIG. 6.—Derivatogram of sodium iodate.

Oxygen evolution starts above 460°, the melt becomes yellow, and at about 510° iodine vapour is produced. Sodium iodide formed during the decomposition remains dissolved.

The amount of iodine removed from sodium iodide was determined by continuous thermal titration[16] under the conditions of the experiments.

It has been stated that iodine is also formed besides oxygen during the thermal decomposition of sodium iodate. The following two reactions take place up to a temperature of 650°:

$$2NaIO_3 = 2NaI + 3O_2$$

$$4NaIO_3 = 2Na_2O + 2I_2 + 5O_2.$$

About 72% of the sample undergoes the first reaction, and 28% the second.

In Table I the temperatures characteristic of the thermal behaviour of the compounds studied are presented.

TABLE I.—SUMMARY OF THERMOANALYTICAL DATA

Figure	Salt	DTA peaks, °C		DTG peaks, °C
		Endothermic	Exothermic	
2	$NaClO_3$	260,790	480,550	480,550
5	$NaBrO_3$	380,760	400	400
6	$NaIO_3$	420,610		610

CONCLUSIONS

In the thermal decomposition of sodium halates, the corresponding sodium halides and gaseous oxygen are produced and also iodine in the case of the iodate. In the solid state, all three compounds studied form an ionic lattice of sodium cations and halate anions.

When the results were evaluated, the polarizing effect of the sodium cation was not taken into consideration, because it exists in all three cases, and only the thermal breaking of the halogen–oxygen bond in the anion was studied in detail. This means that a redox reaction proceeding at high temperature in the melt phase, with transfer of 6 electrons, was investigated.

The shift of melting points towards higher temperatures (260, 380, 420°) in the order chlorate, bromate, iodate, is indicated by the derivatographic curves. In agreement with X-ray investigations, this phenomenon proves that the ionic nature of the compounds increases in the order, chlorate < bromate < iodate.

If the halogen–oxygen internuclear distances determined from X-ray data[17,18] are compared with the values derived as the radius sums, the results presented in Table II can be obtained:

TABLE II

Bond	Measured value, Å	Calculated value, Å	Δ, %
Cl—O	1·43	1·66	16·0
Br—O	1·61	1·79	10·0
I—O	1·86	1·90	2·1

The difference (Δ) between the two values was found to be highest for the Cl–O bond, the value for the Br–O bond being of the same order of magnitude. (Sodium bromate and chlorate are isomorphous; sodium iodate has a different structure.)

Experiments under dynamic conditions show that the decomposition of all three sodium halates is measurable only above the melting point, in the melt phase. During the decomposition of sodium chlorate, sodium perchlorate is formed as an intermediate; no analogous reaction was observed for the other two compounds. The absence of a similar reaction for sodium bromate may be due to the lower temperature of decomposition of sodium bromate.

With sodium iodate, the formation of the periodate is not hindered by the electron configuration of iodine, but probably does not occur because of the high temperature of decomposition and the evaporation of the sodium iodide formed.

According to the DTA curves the decomposition of sodium chlorate and sodium bromate is exothermic, while that of sodium iodate is endothermic. The enthalpy changes indicated by the DTA curves are the resultants of those accompanying three processes; (*a*) breaking of the halogen–oxygen bond, (*b*) formation of the sodium halide, (*c*) solidification of sodium halide.

If the overall equation of the decomposition is considered and the temperature dependence of the heat of reaction neglected, the heat of reaction can be calculated as follows:

$$\Delta H_\gamma^\circ = 2H_{\mathrm{NaX(s)}} - 2H_{\mathrm{fusion(NaX)}} - 2H_{\mathrm{NaXO_3(s)}} - 2H_{\mathrm{fusion(NaXO_3)}}$$

where H = heat of formation, H_{fusion} = heat of fusion, and ΔH_γ° = standard heat of the reaction, all in kcal/mole.

The standard heats of reaction are −28·4, −22·1 and +50·3 kcal/mole for sodium chlorate, bromate, and iodate respectively.

The properties of sodium iodate differ markedly from those of the other two salts. The central halogen atoms in the chlorate and bromate ions have a high polarizing effect owing to the high formal positive charges and small radii of the ions ($\mathrm{Cl^{5+}}$ = 0·26 Å, $\mathrm{Br^{5+}}$ = 0·39 Å), so that they bind $\mathrm{O^{2-}}$ ions by covalent bonds. In the iodate anion the positive charge on the iodine is equal to that on the other two halogens studied, but owing to the larger radius (0·5 Å) the polarizing effect is low. The bonds with $\mathrm{O^{2-}}$ ions are therefore more ionic in nature.

It is interesting that the most ionic of the three halides (sodium chloride) is obtained from the most covalent halate, and the most covalent halide (the iodide) from the most ionic halate.

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Zusammenfassung—Die thermoanalytischen Eigenschaften von Natriumhalogenaten wurden mit einem Derivatographen und einem visuellen DTA-Instrument untersucht. Die untersuchten Verbindungen zersetzen sich merklich nur in der Schmelze, wobei sich die entsprechenden Natriumhalogenide bilden. Bei Natriumchlorat wurde auch Bildung und Zersetzung von Natrium perchlorat beobachtet. Der Vergleich der Ergebnisse thermischer Untersuchungen mit denen röntgenanalytischer Messungen zeigt, daß die chemische Bindung im Natriumjodat den höchsten Ionencharakter zeigt, den geringsten bei Natriumchlorat.

Résumé—On a étudié les propriétés thermoanalytiques des halogénates de sodium au moyen d'un dérivatographe et d'un instrument ATD visuel. On a trouvé que la décomposition thermique des composés étudiés n'a lieu, à un degré mesurable, que dans la phase fondue, tandis que se forment les halogénures de sodium correspondants. Pour le chlorate de sodium, on a pu également observer la formation et la décomposition de perchlorate de sodium. La comparaison des résultats des études thermiques avec les résultats des mesures analytiques aux rayons X montre que le caractère ionique des liaisons chimiques est le plus fort pour l'iodate de sodium et le plus faible pour le chlorate de sodium.

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TEMPERATURE PROFILES IN NITROUS OXIDE SUPPORTED ACETYLENE FLAMES AT ATMOSPHERIC PRESSURE

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Summary—Temperature profiles have been established at three mixture strengths of the nitrous oxide-acetylene flame used in atomic-absorption spectroscopy. Measurement of the electronic excitation temperature of the red-feather zone by the sodium line-reversal and iron two-line methods yields average maximum temperatures of 3070 and 3025 ±50°K respectively. This is significantly lower than the only previously reported value, 3228°K. Other temperature measurements obtained by studying intensity distribution of NH rotational fine structure and CN vibrational structure yielded less precise results, but suggest a state of thermal equilibrium in the flame. The temperature gradient within the flame shows a steady decrease with height above the primary zone. A study of CN spectra and the zones of persistence of free atoms and of metal oxide species suggests a mechanism of free atom production within the cyanogen zone whereby the removal of oxidizing radicals by CN promotes dissociation of metal oxide species previously formed in the primary zone of the flame.

IN A PREVIOUS paper from this laboratory we reported a study of the emission spectra of premixed flames of nitrous oxide with acetylene in the presence of a range of refractory oxides.[1] The effectiveness of this flame for the determination by atomic-absorption spectroscopy of several elements forming refractory oxides (*e.g.*, aluminium, titanium and molybdenum) arises from the production of a higher population of free metal atoms in the ground state in this flame than in the conventional air–acetylene flame. Little evidence has been presented, however, to explain the maintenance of appreciable populations of atoms of these elements in this flame. It is noteworthy that for most elements of this type, good sensitivity in absorption is obtained only in flames which are fuel-rich (reducing) in character. As reported previously, the high population of the CN radical found in these flames appears to create a reducing atmosphere in which free atoms of the elements are produced and maintained. The variation in temperature in various zones of the flame burning at different mixture strengths has an important bearing on the sensitivities obtainable in absorption and emission spectroscopy in the flame, and also on any mechanism postulated to account for the production and maintenance of free metal atoms in the plasma. The maximum temperature of the nitrous oxide–acetylene flame burning at atmospheric pressure has been reported as 2955°C.[2] This is the sole value available in the literature, and if it is a value obtained practically, rather than a calculated value of the maximum thermodynamic temperature, no facts are available concerning the type of burner at which the flame was supported, or the mixture conditions or region of the flame which produce this value. We have, therefore, made a study of the temperature profiles found in a premixed nitrous oxide–acetylene flame burning under different mixture conditions at a 5-cm burner of the type commonly used for atomic-absorption measurements.

If the flame gases are not in equilibrium it is difficult to define the "temperature" of the system. As noted by Gaydon and Wolfhard,[3] however, departures from equilibrium are slight for the interconal or burnt gases of most small, steadily burning premixed flames, and there is a real need, for the purposes mentioned, to establish the temperature in these regions. It is necessary to obtain "population" temperatures for various flame species and types of energy (electronic, vibrational and rotational) within the system. When these result in a common temperature within experimental error by various means of measurement, the system may be considered to be in thermal equilibrium and may be assigned a temperature. This paper reports the results obtained by the line-reversal method and two-line method for the effective electronic excitation temperatures for sodium and iron, respectively. We have also made estimates by emission spectrography of the effective rotational temperature of NH and the effective vibrational temperatures of CN in the flame gases of the fuel-rich nitrous oxide–acetylene flame above the primary reaction zone.

EXPERIMENTAL

Burner arrangement

The burner arrangement was similar to that previously described.[1] The burner head was constructed of stainless steel and consisted of two steel plates bolted to a massive steel head to form a slit 0·375 mm wide and 5 cm long. The burner head was mounted on a stainless steel base and premixing chamber similar to that in the air–acetylene burner used on the Unicam SP 900A flame spectrophotometer. The burner was lit on air–acetylene, and the change to nitrous oxide–acetylene effected by gradual replacement of the air by nitrous oxide *via* a T-piece and two rotameters. The sample solutions were introduced into the flame as aqueous $10^{-2}M$ sodium or iron(III) chloride solutions *via* a nebulizer and glass expansion chamber. Aspiration was by the nitrous oxide supply to the flame.

Sodium line-reversal method

The background continuum source used was provided by the anode of a d.c. arc burning at pure carbon electrodes (Johnson and Matthey Ltd., London). The diameter of the anode was 6·5 mm, and the arc was run at 10 A. With the electrode assembly used and a 10-mm arc gap, the voltage drop was 60 V. The effective temperature of the background radiation from the anode under these conditions was determined by direct measurement, with a potentiometer (National Physical Laboratory calibration) circuit, of the radiation from the anode spot, received at the face of a calibrated standardized thermopile. The average value obtained in this way for the anode temperature was 3772°K.

The radiation from the anode was focused into the flame through a quartz lens (diameter 25 mm, focal length 50 mm). The loss of radiation from the background by reflection at the air-glass interfaces of this lens was estimated by measurement of the apparent temperature of the anode with and without the lens in position; it was found to be 8·8%. The radiation from the flame was focussed by a quartz lens (diameter 25 mm, focal length 75 mm) onto the plane of the slit of a small table spectroscope (Beck, London). The intensity of the radiation from the anode spot was reduced with a rotating sector of variable aperture, set between the arc and flame, and driven at constant speed by a synchronous motor.

To make a temperature measurement by this method, a solution of sodium chloride ($10^{-2}M$) was nebulized into the flame. The arc discharge was initiated and the background brightness at *ca.* 5850–5950 Å viewed through the spectroscope, a narrow slit being used. Under these conditions the sodium 5890 Å doublet was seen in absorption against the background. The rotating chopper was then set to narrow aperture and rotated in front of the lens. The sodium doublet was then seen in emission against the background. The aperture of the rotating chopper was then increased stepwise until the sodium doublet was not visible either in emission or absorption, *i.e.*, the brightness temperatures of both background and flame emission were the same at this wavelength. The rotating sector and drive motor were then removed from the optical bench and the effective aperture was determined at this "balance" setting. This was accomplished by interposing the sector between a standard tungsten ribbon filament lamp (Mazda projection lamp, Type R/1, 6 V, 108 W) operated at stabilized controlled current, and the calibrated thermopile and potentiometer. The attenuated radiation from the tungsten lamp was received and measured at the thermopile. The aperture of the rotating sector at the established "balance" setting was then determined by relating the value obtained in this calibration procedure to a prepared graph of energy received at the thermopile *vs.* aperture of the rotating sector (or degree of attenuation of the background brightness temperature). Thus the temperature of the attenuated background and flame was obtained.

Two-line method

A Hilger large quartz spectrograph was used for these measurements, and the arrangement of apparatus was similar to that described previously.[1] The burner was mounted on the optical bench so that it was "end-on", *i.e.*, an image of the flame from the 0·375-mm side of the burner was presented to the spectrograph and focussed at the slit by a quartz lens. In this way an inverted full-size image of selected parts of the flame was obtained vertically along the slit. Spectrograms obtained in this way show the variation of emission intensity with height, at wavelengths characteristic of species in the flame. Care was taken to recognize the possibility of self-absorption of radiation from the flame species when the burner was used in this position. Exposures were made on B10 or R40 plates, depending on the wavelength range to be examined and the speed required. Calibration of the plate emulsion at the wavelengths used was achieved with a Hilger stepped sector which gives intensity ratios of 1:2:4:8:16:32. The plates were standardized for variation in emulsion sensitivity at the wavelengths of the iron spectral lines to be compared, by using a tungsten ribbon-filament lamp operated at a known brightness temperature (1650°K). This source approximates to a black body radiator, so its relative output intensity may be calculated at the wavelengths concerned. The spectral lines of which the intensities were compared for the temperature measurements were all within 100 Å of each other, and the correction for change in plate sensitivity over this range proved negligible. The plates were developed in Ilford ID 36 developer under standardized conditions, and intensities were measured with a Hilger photomicrodensitometer. The same burner and nebulizer arrangement was employed as in the line-reversal method.

RESULTS

Line-reversal method

The line-reversal method, which is well-known and often used for flame temperature measurement, was first described by Kurlbaum.[4] The determination of flame temperatures by this method has been reviewed by Gaydon and Wolfhard.[3] The strip-filament tungsten lamp is the background source most frequently used for determination of the temperature of air-supported flames. The highest temperature available from this source, however, is *ca.* 2700°K, and at this temperature the lamp requires frequent standardization and the life-time of the tungsten filament is very short. The highest temperature available is also inadequate for hot oxygen–hydrocarbon flames, and in these studies also proved inadequate for the nitrous oxide–acetylene flame. We have used a d.c. carbon arc as the high temperature background source. The anode of this arc performs very nearly as a black body radiator, and its mean temperature was determined directly with a calibrated thermopile as 3770 ± 30°K. Henning and Tingwaldt[5] and Krygsman[6] found the temperatures of the anodes of similar arcs to be 3818°K and 3800°K respectively for the visible region of the spectrum.

When a carbon-arc source is employed with sodium in the flame, a correction must be applied for loss of light from the background source at the first lens by reflection before it enters the flame. This was achieved by determination of the energy received at the calibrated thermopile in the presence and absence of the lens. The mean correction found by this method was 8.8%, and background temperatures were corrected by this amount in all further measurements.

Owing to the fact that with the apparatus used the radiation from the background was focused to a circle of 5 mm diameter in the flame, and also because relatively large temperature gradients exist in the flames, the values obtained are average temperatures in circular areas of the flame, 5 mm in diameter. The reversal method was applied at different heights in fuel-lean, slightly fuel-rich and very fuel-rich nitrous oxide-acetylene flames. The results obtained are shown in Table I.

TABLE I.—TEMPERATURE VALUES OBTAINED

Height above burner plate, *mm*	Fe two-line method			Na line-reversal method	
	Line-pair used Å	Temp., °*K*	Average for zone, °*K*	Temp., °*K*	Average for zone, °*K*
Slightly lean N_2O–C_2H_2 flame (N_2O—5·6 l/min; C_2H_2—2·6 l/min)					
3·5	3749–3705	2930			
	3749–3722	2950			
	3758–3722	2940	2940		
7·5	3749–3705	2850			
	3749–3722	2855			
	3758–3722	2845	2850		
15	3749–3705	2800		2565	
	3749–3722	2775		2590	
	3734–3748	2830		2590	
	3758–3733	2800		2605	
	3820–3824	2785	2800	2535	
				2530	
				2600	
				2555	
				2575	2570
Slightly fuel-rich N_2O–C_2H_2 flame (red feather) (N_2O—5·6 l/min; C_2H_2—3·0 l/min)					
4·5	3647–3679	3040			
	3749–3705	3100			
	3749–3722	3020		2945	
	3749–3705	2990		3055	
	3749–3722	2930		3090	
	3758–3705	3100		3155	
	3758–3722	3045		3005	
	3758–3733	2955	3025	3055	
				3005	
6	3749–3705	2880		3040	
	3749–3722	2890		3125	
	3734–3733	2940		3160	
	3749–3705	2920		3130	3070
	3749–3722	2880			
	3749–3722	2890			
	3749–3722	2890	2900		
7·5	3749–3705	2840			
	3749–3722	2820			
	3749–3705	2820			
	3749–3722	2810			
	3749–3705	2810			
	3749–3722	2875			
	3749–3705	2875			
	3749–3722	2825			
	3749–3705	2820			
	3749–3722	2830			
	3734–3748	2825	2830		
12	3734–3748	2785			
	3749–3733	2815			
	3749–3705	2830			
	3749–3722	2810	2810		
17	3749–3705	2800			
	3749–3722	2770			

TABLE I *continued*

Height above burner plate *mm*	Fe two-line method: Line-pair used Å	Fe two-line method: Temp., °*K*	Fe two-line method: Average for zone, °*K*	Na line-reversal method: Temp., °*K*	Na line-reversal method: Average for zone, °*K*
	3734–3748	2760		2780	
	3749–3705	2780		2730	
	3749–3722	2760		2675	
	3734–3748	2765		2780	
	3734–3748	2750		2815	
	3820–3824	2760		2775	
	3734–3748	2770		2745	2755
	3749–3722	2775			
	3820–3824	2760			
	3749–3705	2785			
	3734–3748	2785	2770		
	3749–3722	2775			
	3820–3824	2780			
35	3734–3748	2740		2640	
	3734–3748	2725		2590	
	3749–3705	2745		2565	
	3749–3722	2735		2520	
	3734–3748	2735		2585	
	3820–3824	2730		2570	
	3825–3878	2720	2730	2555	2575
55	3734–3748	2700			
	3820–3824	2705			
	3825–3878	2710	2705		
70	3734–3748	2690	2690		
Fuel-rich N_2O–C_2H_2 flame (luminous) (N_2O—5·6 l/min; C_2H_2—3·7 l/min)					
12	3749–3705	2830		2785	
	3749–3722	2840			
	3758–3733	2860		2745	
	3825–3878	2885	2855	2760	
17	3734–3748	2730		2780	
	3749–3705	2615		2760	
	3749–3722	2810		2760	2765
	3820–3824	2750			
	3749–3722	2775			
	3820–3856	2820	2750		
30	3734–3748	2750		2570	
	3749–3705	2750		2590	
	3749–3722	2715		2600	
	3820–3824	2715	2730	2555	
				2570	2580
50	3749–3722	2700			
	3820–3824	2710			
	3749–3705	2750	2720		

The precision of the line-reversal method as conducted with the apparatus described here is governed largely by the stability of the background anode spot temperature and the reproducibility with which the point of balance for background and flame radiation can be detected visually. From the range of values obtained for each zone, the relative standard deviation in each set of results is 1–2% in the temperature range encountered. For the very important region of the flame immediately above the primary zone this amounts to an error of ±50°K.

Two-line method

This method was developed by Ornstein and co-workers[7,8] for the measurement of arc temperatures and electronic transition probabilities. When thermal equilibrium prevails within the system under investigation, for any two lines in the emission spectrum of an element introduced into the system we may write

$$\frac{I'}{I} = \frac{A' \,.\, g' \,.\, \nu' \,.\, \exp\,(-E'/kT)}{A \,.\, g \,.\, \nu \,.\, \exp\,(-E/kT)} \tag{1}$$

where A and A' = transition probabilities for the lines, g and g' = statistical weights of the states, ν and ν' = frequencies of the lines, E and E' = excitation energies, k = the Boltzmann constant and T = the absolute temperature. Thus when the intensities, statistical weights and energy levels of the two lines are known, it is possible to calculate either the absolute temperature of the source *or* the ratio of the transition probabilities, provided that the other variable is known. The procedure most commonly adopted is to establish the required transition probabilities by using a source of known temperature, and subsequently to employ these values to evaluate the temperature of other sources. It is possible to apply this general equation and method to atomic or molecular spectra. When the temperature T is deduced from the relative intensities of rotational lines within the same vibrational band system of a molecular species in the flame, the value obtained represents a measure of the population ratios of rotational levels, and is termed a "rotational temperature". Similarly, when the temperature T is obtained for a molecular species from the intensities of different vibrational bands within a single electronic transition, it measures population ratios of vibrational levels and is termed a "vibrational temperature" for that species We have principally been concerned with the effective atomic "electronic temperatures", *i.e.*, values for population ratios of electronically excited states of the metal atom introduced into the flame.

Iron was selected as the most suitable element for measurement of the effective electronic temperature of the nitrous oxide–acetylene flame by the two-line method. Owing to the possibility of self-absorption, the two-line method is not usually used with resonance lines. Consequently the element chosen must exhibit at the expected temperatures a series of non-resonance lines at wavelengths which are free from interference from the flame background emission. The transition probabilities of a large number of such lines for iron are well-known. It was decided to accept established literature values for the transition probabilities,[9,10] as their accurate measurement in a source of known temperature was not feasible with the apparatus available. The wavelengths of the iron lines emitted by the flame may be assigned with certainty by inclusion of a reference spectrum from an iron arc on each plate, and comparison of this arc spectrum and the flame spectrum with a standard iron arc spectrum. Of the 17 iron lines used, only those at 3679·9 and 3824·4 Å are resonance lines.

In order to establish that the experimental conditions, plate calibration and standardization, and transition probabilities were reliable, the temperatures of the interconal zones of air–acetylene and oxy-hydrogen flames were determined by this method. The temperature profiles within these flames have been studied by several workers[11–15] and are well established. The temperature above the primary zone of the premixed stoichiometric air–acetylene flame is well established as *ca.* 2500°K, and the values available compare well with the calculated value for this flame, 2520°K.[16,17] By the two-line method with iron we obtained an average value of 2490°K for this flame flame burning at the 5-cm burner described. Similarly we obtained an average value of 2700°K for the effective electronic excitation temperature for iron in the turbulent stoichiometric oxy-hydrogen flame burning at a total-consumption nebulizer-burner. This value compares favourably with the values obtained by other workers[14,18] for similar flames aspirating aqueous solutions (which cool the turbulent flame considerably). The calculated maximum temperature for the *dry* oxy-hydrogen flame has been quoted as 2953°K and 2993°K.[20,21]

The values we have obtained by the two-line method with iron for the nitrous oxide–acetylene flame at different mixture strengths are shown in Table I. It is not possible to obtain reliable temperature values immediately above the primary zone of very fuel-rich flames by this method, owing to the high background emission produced as a continuum by the carbon luminosity in this region. In the same manner the background due to the chemiluminescence of the reaction $CO + O \rightarrow CO_2 + h\nu$, is appreciable high up in the fuel-lean flame and prevents the measurement of very accurate temperature values in this region.

Apart from the dependence of the precision on other experimental parameters in this method, any error in the measurement of the ratio I'/I or $A'g'/Ag$ will produce errors in the temperatures obtained. Broida[19] has expressed the relative error, $\Delta T/T$, as $\Delta T/T = kT\Delta r/r(E' - E)$, where Δr is the error in the measurement of the ratio r of the intensities or transition probabilities. For example, a typical value of $E' - E$ is 0·75 eV and ratios can be measured such that $\Delta r/r$ is 0·05 or less under favourable conditions. Since $k = 8{\cdot}616 \times 10^{-5}$ eV/deg, for a gas at 3000°K, $\Delta T/T = 1{\cdot}7\,\%$, *i.e.*, $\Delta T = 50$°K. When many values are established from use of different line pairs, quite good precision and accuracy can be obtained.

Rotational and vibrational temperatures

Values have been estimated for the effective rotational temperature for NH and the effective vibrational temperature for CN in the "red-feather" zone of the slightly fuel-rich nitrous oxide–acetylene flame. These values were obtained from spectrograms of the flame with the same burner arrangement and flow-rates of nitrous oxide and acetylene as for the two-line method in the slightly fuel-rich flame. The NH rotational temperature was obtained from the emission of the strongest (0, 0) sequence of NH at 3360 Å ($^3\Pi - {}^3\Sigma$). This band has fairly open rotational fine structure and is well separated from other band systems. The *Q* branch is unresolved, but the effective rotational temperature for NH can be estimated from the intensity distribution of the rotational lines in either the *P* or *R* branches. Values obtained from location of the position of maximum intensity, and by the equal intensity method[3] in the R branch, yield an average rotational temperature for NH of 3600 ± 300°K. The values obtained are not very precise, and the methods we have employed may not be very accurate. The limitations of the apparatus available did not render worthwhile the application of more sophisticated methods of rotational temperature measurement. The average value obtained, however, compares very well with the value of 3700°K found by Gaydon[22] for a stoichiometric nitrous oxide–acetylene flame burning at a different type of burner.

The effective CN vibrational temperature was estimated from the ratio of the maximum intensities of bandheads within the CN sequences at 3590 Å (1, 0), 3883 Å (0, 0) and 4216 Å (0, 1). The required CN vibrational transition probabilities were taken from the data of Fraser, Jarmain and Nicholls.[23] The average of the series of values obtained for the CN vibrational temperature was 3450 ± 300°K.

The temperature results for NH and CN are probably of limited accuracy, principally owing to the fact that the spectrographic equipment employed was only of moderate resolution. The results obtained are higher than the electronic excitation temperatures for iron and sodium, and the calculated equilibrium temperature for the stoichiometric flame. These results suggest, however, that in the reducing zone of the slightly fuel-rich flame any departure from equilibrium which occurs is slight.

DISCUSSION

The results for both the line-reversal and two-line methods indicate maximum temperatures immediately above the primary zone of the nitrous oxide–acetylene flame which are significantly lower than the maximum value of the flame temperature quoted in the literature[2] as 2955°C. The temperature attainable by the stoichiometric nitrous oxide–acetylene flame may be calculated by the method of Damköhler and Edse,[24] and is 2930°C (3203°K) in the burnt gases above the reaction zone, the dissociation of the products being allowed for. The difference between this value and the values obtained practically for the slightly fuel-rich flame amounts to *ca.* 200°K. The temperature of the slightly fuel-rich flame would be expected to be somewhat different from that of the stoichiometric flame, but probably not by as much as 200°K. The lower maximum temperatures obtained practically are best explained by the fact that in each case the flame is cooled somewhat by the massive steel burner plate employed, and also because in both methods by which the electronic excitation temperatures were obtained the flame was cooled to some extent by the aqueous solutions which were introduced into the flame.

The results for the line-reversal method are, as stated previously, average values for areas in the flame, of the diameter of the image of the anode spot in the flame. It is, therefore, difficult to construct meaningful temperature *vs.* height profiles for the reversal results. The variation of temperature with height at the three different mixture strengths examined by the two-line method is shown in Fig. 1. These profiles are relatively smooth, and show a steady fall in temperature above the primary reaction zone for each of the mixtures examined. From the point of view of analytical flame spectroscopy the most important part of the flame is the region immediately above the primary reaction zone. In this region no appreciable difference in the practical temperature values occurs between the lean, slightly rich and very rich flames. Thus in the slightly fuel-rich flame commonly used for atomic-absorption spectroscopy, the maximum temperature occurs immediately above the primary reaction zone and then decreases steadily throughout the red zone and above it.

From the results obtained in this investigation it appears that the red zone of the slightly fuel-rich flame is in a state of thermal equilibrium. This finding assists in the interpretation of the emission and absorption characteristics of metal atoms introduced into the flame plasma. In a previous paper[1] we observed that for elements such as molybdenum and aluminium pronounced atomic line emission persists only as high in the flame as the CN band emission (*i.e.*, the reducing atmosphere). From the sharp drop in line emission intensity which occurs for these elements immediately

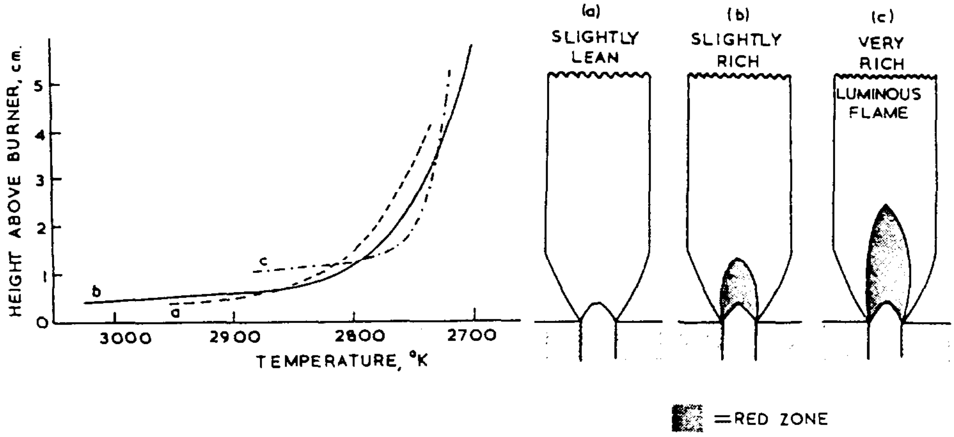

FIG. 1.—Temperature *vs.* height profiles obtained in two-line method, and flame appearance.
(a) Slightly lean flame, (b) slightly rich flame, (c) very fuel-rich flame.

above the red zone, it appears that the maintenance of the metal atom population is controlled by the reducing conditions as well as by the temperature of the flame. This suggestion is obviously only tenable if no sharp fall in temperature occurs at the boundary between the reducing red zone and the outer oxidizing mantle. The results of this study reveal a steady fall in temperature throughout the red zone and above it in the flame, and no such sharp drop in temperature is observed. The evidence available from atomic-absorption studies, which provide a more direct measure of the variation in metal atom population with height in the flame, also supports the view that a rapid decrease in metal atom population occurs at the top of the red zone. Also the results of our original spectrographic studies[1] suggest that a rise in metal oxide population occurs immediately above the red zone for elements such as aluminium, titanium and beryllium.

In the reducing atmosphere in fuel-rich flames, the partial pressure of atomic oxygen, p_O, and the partial pressures of other oxidizing species, p_{OH} and p_{H_2O}, are greatly depleted. Amongst others, reactions of the following type may account for the consumption of oxidizing species;

$$CN + O \rightarrow CO + \tfrac{1}{2}N_2$$

$$CN + OH \rightarrow CO + \tfrac{1}{2}N_2 + \tfrac{1}{2}H_2$$

$$CN + H_2O \rightarrow CO + \tfrac{1}{2}N_2 + H_2$$

Mavrodineanu[25] has suggested that the presence of gaseous metal oxides in flames may be accounted for by the equilibria:

(1) $$M + O \rightleftharpoons MO \qquad K_1$$

(2) $$M + OH \rightleftharpoons MO + H \qquad K_2$$

(3) $$M + H_2O \rightleftharpoons MO + H_2 \qquad K_3$$

The dissociation of the metal oxides is therefore promoted when the partial pressures of oxidizing species are lowered. For example, in reaction (1), if K_1 is the equilibrium constant, the partial pressure of free metal atoms p_M is given by $p_M = K_1 \cdot p_{MO}/p_O$, where p_{MO} and p_O are the partial pressures of metal oxide and atomic oxygen, respectively. The partial pressure of free atoms, p_M, may be expressed in terms of their number, N, by $p_M = NkT$, where k is the Boltzmann constant and T the absolute temperature. Thus the number of free atoms can be expressed by $N = K_1 p_{MO}/kTp_0$. In atomic-absorption spectroscopy the integrated absorption coefficient, k_ν, at frequency ν is proportional to the number of free atoms, N, capable of absorbing at this frequency: $\int k_\nu . d\nu = BN$, where B is a constant depending on quantities related to the absorption line. Substituting for N we obtain

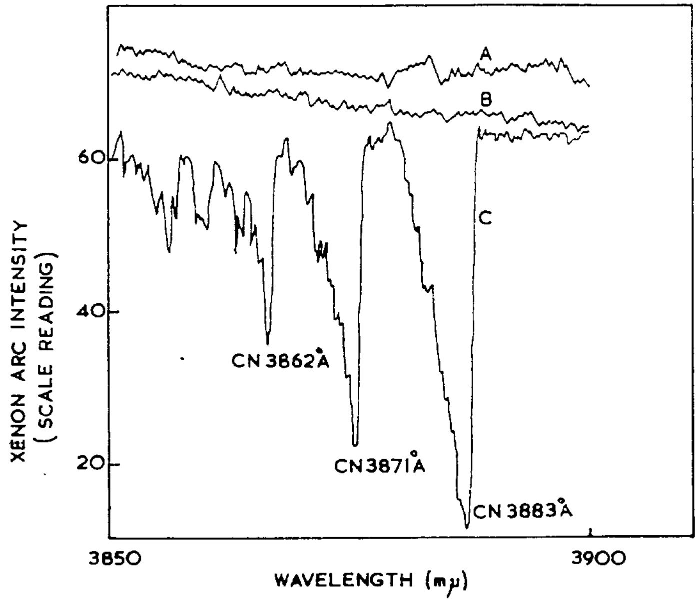

FIG. 2.—Spectrum showing absorption by CN at the (0, 0) sequence of the CN violet band system at 3883 Å, against the background continuum from a high pressure xenon arc. (*A*) Xenon arc background alone (no flame), (*B*) background arc spectrum viewed through slightly fuel-lean flame above primary zone, (*C*) background arc spectrum viewed through fuel-rich flame above primary zone.

$$\int k_\nu . d\nu = BK_1 p_{MO}/kTp_0.$$

This equation shows how the integrated absorption coefficient may be expected to vary with the oxidizing or reducing nature of the flame plasma for elements which form gaseous oxides in the flame. This interpretation of the processes which result in the existence, in the reducing nitrous oxide–acetylene flame, of appreciable populations of free atoms of elements forming refractory oxides depends on the production of a partial pressure of gaseous metal oxide in the flame. Thus the sensitivity obtainable in atomic-absorption spectroscopy will depend on the partial pressure of metal oxide which can be produced at the flame temperature, and on the dissociation energy of the oxide. The low sensitivity obtained for elements such as niobium, tantalum and zirconium even in the hot, reducing nitrous oxide–acetylene flame may be explained by the extremely stable and involatile nature of their oxides.

Our earlier observations on thermal emission by CN suggested that it plays an important role in the flame processes above the primary zone. It is thus necessary to have evidence that an appreciable concentration of CN is present in this region. The intense CN emission alone is not sufficient evidence of this, although the results reported here suggest that the flame gases in this region are in thermal equilibrium. The value obtained for the effective CN vibrational temperature does not differ sufficiently from the sodium and iron electronic and NH rotational temperatures obtained to lead us to suppose that over-excitation contributes appreciably to the CN emission. Perhaps the best evidence for the existence of a relatively high CN population in the ground state is shown in Fig. 2. This shows the facile detection of CN in absorption above the primary zone in the slightly fuel-rich flame, against the background continuum radiation from a high-pressure xenon arc. It is noteworthy that CN was not detected in absorption above the primary zone of the slightly fuel-lean flame. Figure 3 shows the way in which the absorption by CN at the (0, 0) sequence of the CN violet band system at 3883 Å, against the xenon arc background, varies with the acetylene flow-rate. The CN concentration increases steadily as the flame becomes increasingly fuel-rich. In very fuel-rich luminous flames no further increase in CN absorption occurs when the acetylene flow-rate is increased, possibly owing to the lack of sufficient nitrogen from nitrous oxide in the primary reaction zone for its formation under these conditions. The excess of fuel in very rich mixtures is then converted mainly into carbon, the luminosity of which imparts to the flame its characteristic appearance.

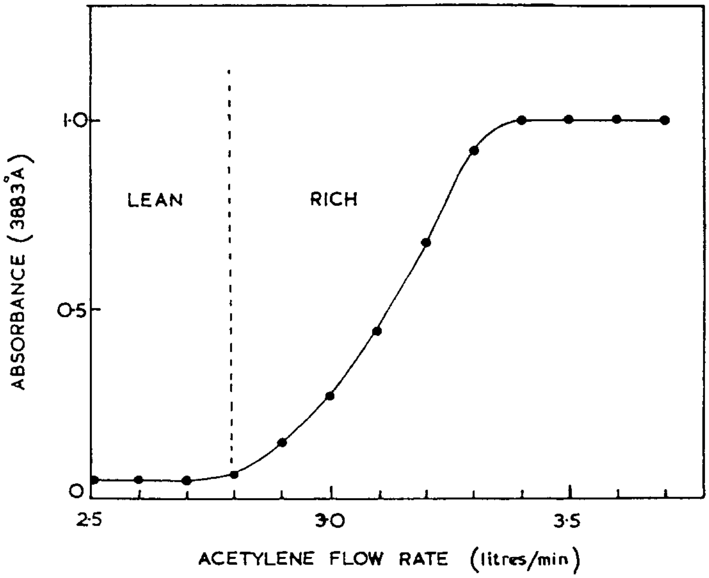

FIG. 3.—Effect of fuel flow-rate on absorption by CN at the (0, 0) sequence of the CN violet band system at 3883 Å.

Acknowledgement—We are grateful to the Ministry of Technology for support of this programme.

Zusammenfassung—Die Temperaturprofile der in der Atomabsorptionsspektrometrie verwendeten Lachgas-Acetylen-Flamme wurden bei drei Mischungsverhältnissen ermittlet. Die Messung der Elektronenanregungstemperatur im roten Saum mit den Methoden der Natriumlinienumkehr und der zwie Eisenlinien ergab mittlere Maximaltemperaturen von 3070 bzw. 3025 ± 50°K. Das ist beträchtlich niedriger als der einzige bisher mitgeteilte Wert von 3228°K. Andere Temperaturmessungen durch Untersuchung der Intensitätsverteilung der NH-Rotationsfeinstruktur und CN-Schwingungsstruktur ergaben weniger genaue Ergebnisse, deuten jedoch auf einen Zustand thermischen Gleichgewichts in der Flamme. Das Temperaturgefälle in der Flamme zeigt ein stetiges Abfallen mit der Höhe über der Primärzone. Eine Untersuchung der CN-Spektren und der Zonen, wo länger lebende freie Atome und Metalloxidspezies vorliegen, deutet darauf hin, daß in der Dicyanzone freie Atome gebildet werden, wobei das Abfangen oxidierender Radikale durch CN die Dissoziation der ursprünglich in der Primärzone der Flamme gebildeten Metalloxidspezies begünstigt.

Résumé—On a établi les profils de température pour trois concentrations de mélange de la flamme protoxyde d'azote-acétylène utilisée en spectroscopie d'absorption atomique. Les mesures de la température d'excitation électronique de la zone rouge du fuseau aplati par la méthode de renversement de la raie de sodium et la méthode à deux raies du fer donnent des températures maximales moyennes de 3070 et 3025 ± 50°K respectivement. Ceci est notablement plus faible que la seule valeur rapportée antérieurement, 3228°K. D'autres mesures de température obtenues en étudiant la répartition d'intensité de la structure fine de rotation de NH et de la structure de vibration de CN donnent des résultats moins précis, mais suggèrent un état d'équilibre thermique dans la flamme. Le gradient ce température dans la flamme montre une décroissance constante avec la hauteur au-dessus de la zone primaire. Une étude des spectres de CN et les zones de persistance d'atomes libres et d'espèces oxyde métallique suggérent un mécanisme de production d'atomes libres à l'intérieur de la zone cyanogène, par lequel l'élimination de radicaux oxydants par CN provoque la dissociation de l'espèce oxyde métallique antérieurement formée dans la zone primaire de la flamme.

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STUDIES IN ATOMIC-FLUORESCENCE SPECTROSCOPY—VII

FLUORESCENCE AND ANALYTICAL CHARACTERISTICS OF ARSENIC, WITH A MICROWAVE EXCITED ELECTRODELESS DISCHARGE TUBE AS SOURCE

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Summary—The construction of an electrodeless arsenic discharge tube and its use for atomic-fluorescence studies is described. Cool nitrogen-hydrogen and argon-hydrogen diffusion flames as well as normal premixed flames are considered as atom reservoirs and the atomic-fluorescence emission at 15 different wavelengths is evaluated. The diffusion flames give the largest emission signals at arsenic concentrations below 200 ppm, but show a premature curvature at higher concentrations because of the presence of an abnormally high density of arsenic atoms. Above 200 ppm of arsenic, the premixed air-acetylene flame is superior. The limit of detection at 1890 Å is 0·2 ppm of arsenic in the nitrogen-hydrogen diffusion flame and 1·0 ppm in the air-acetylene flame. A long path-length diffusion flame is also particularly useful in atomic-absorption measurements because it absorbs very little radiation in the far ultraviolet region and gives an abundance of arsenic atoms.

The determination of arsenic by flame emission spectroscopy presents many difficulties because the lowest energy resonance line requires an excitation energy of over 6 eV, which is unobtainable with normal flames. Emission studies[1] have, however, been made recently by measuring the chemiluminescence in the reaction zone of an oxy-acetylene flame whilst aspirating with organic solvents. Under these particular conditions a limit of detection of 2·2 ppm at 2350 Å was obtained. Similarly, Gilbert[2] has observed the chemiluminescence spectrum from isopropanol solutions of arsenic nebulized in an air-hydrogen flame.

Arsenic hollow-cathode lamps give a low radiation output at the resonance wavelengths (1890, 1937 and 1972 Å) and are difficult to prepare owing to the volatility of arsenic, which also causes a short operating life. In spite of these limitations, successful atomic-absorption studies have been made by Slavin *et al.*[3] using a hollow cathode lamp at 1937 Å. The 1890 Å resonance line was regarded as giving the strongest absorption, but there was less noise at the 1937 Å resonance line because of its apparently higher intensity (as detected by the photomultiplier). The limit of detection for 1% absorption was given as 2 ppm.

This paper reports the determination of arsenic by atomic fluorescence and atomic-absorption spectroscopy in premixed and diluted diffusion flames.

EXPERIMENTAL

Apparatus

The apparatus used in our studies consisted of a Unicam SP 900A atomic-absorption/flame-emission spectrophotometer coupled to a Servoscibe recorder used on the 0–10 mV range. A description of its use for atomic fluorescence measurements has been given elsewhere.[4] The electrodeless discharge tubes were prepared by using the apparatus described in a previous communication[5] and the discharge was maintained by using a Microton 200 microwave generator (2450 ± 25 Mc/s) and a model 214L resonant cavity (Electro-Medical Supplies). The discharge was initiated with a high-frequency "Tesla" vacuum-tester.

Preparation of microwave excited electrodeless discharge tubes

More difficulties were encountered in the preparation of a stable arsenic tube with an intense discharge than those experienced in previous work.[5-8] Quartz tubes 3·5 cm long containing *ca.* 10 mg of arsenic metal (≡1 mm Hg pressure at 372°) and less than 0·5 mm Hg pressure of argon gave a green coloured arsenic discharge. However, free arsenic plated out on the walls of the tube within the cavity, and the ends of the tube became quite hot during operation; this behaviour is the reverse of that normally observed. The arsenic lines were quite intense when the tube was operated at 40 W, but the stability was very bad owing to the plating out of the arsenic. Tubes containing more than 1·0 mm Hg pressure of argon initially gave a very intense, stable, blue arsenic discharge at 35 W, but after *ca.* 2 hr of operation, the discharge transiently increased in intensity, changed to a light green colour and then abruptly to a red–violet (argon) discharge. This type of discharge remained even on increasing the power to 75 W. If the tube was now heated and again initiated with a "Tesla" coil, the blue arsenic discharge was again obtained. This now only lasted for about half an hour before changing to green and finally reverting to a normal argon discharge. The length of time that the blue discharge would remain became less after successive heatings and finally would last for no more than 1 min. This curious effect is difficult to explain, but could be connected with the amorphous arsenic used, which slowly changes to a less volatile more stable allotrope under these low pressure conditions. The heating process could reveal a fresh amorphous arsenic surface as long as any remained. No evidence of arsenic attack on the quartz was observed.

Quartz tubes 3·5 cm long, containing various amounts of arsenic and sulphur and 0·1–0·5 mm Hg pressure of argon gave an intense arsenic discharge, but after 1–2 hr operation at *ca.* 35 W the discharge went out and could not be reinitiated. Again no evidence of attack on the quartz was observed. We have not been able to explain the failure of these particular tubes.

Quartz tubes 3·5 cm long, containing hydrogen as the filler gas, were also made and were operated at *ca* 30 W. When the hydrogen pressure was less than 2 mm Hg, severe plating-out occurred after about 1 hr of operation. However, for hydrogen pressures $\gg$5 mm Hg, little plating-out occurred as long as the tube was not overcooled. Quite stable discharges were obtained at 10–15 W with no cooling. Although these tubes gave the arsenic spectrum, it was not very intense and they were only used for some atomic-absorption measurements. Tubes containing 5 mm Hg pressure of hydrogen and 2 mm Hg of argon gave more intense arsenic discharges than those tubes containing only hydrogen. The arsenic became white–brown in the hydrogen-filled tubes and black in the argon-filled tubes. A tube containing arsenic and mercury gave only a very weak arsenic discharge.

The best sources were made in tubes 4 cm long, using a mixture of arsenic and iodine in the weight ratio 2:1 and an argon pressure of *ca.* 1 mm Hg. These tubes gave a stable intense arsenic discharge when run at *ca.* 30 W with only very slight cooling or none at all. At powers >35 W, instability occurred because of an increase in pressure within the tube. If the iodine:arsenic ratio was increased, the tube gave a predominantly iodine type of discharge, thereby showing that the metal was not in excess.

Procedure[5]

A 4-cm quartz bulb was degassed under vacuum at bright red heat for *ca.* 10 min during which time it was periodically flushed with argon to remove impurities. The tube was allowed to cool to room temperature and was removed from the vacuum line, and then about 15 mg of arsenic metal (99·999% purity) were introduced into the bulb. The tube was reconnected to the vacuum line, evacuated and flushed out with argon. A piece of wet asbestos rope was tied round the centre of the bulb and the arsenic in the bottom of the tube was gently heated with a microburner so that it sublimed 1–2 cm up the tube. This process was designed to remove any occluded gases or moisture in the arsenic. After cooling to room temperature, the tube was removed from the vacuum line and *ca.* 8 mg of iodine were added. The tube was again connected to the vacuum line, evacuated, flushed out with argon and pumped down to a pressure of about 0·1 mm Hg. The tube was left in this condition for about 5 min whilst being continuously pumped in order to volatilize any moisture in the iodine. Then a pressure of 1 mm Hg of argon was introduced into the system and the bulb was sealed off.

Discharge tube characteristics

The ground state of the arsenic atom is a $^4S_{1\frac{1}{2}}$ state and all the lines shown in the Grotrian diagram presented by Candler[9] were obtained, as well as some higher state lines which are accounted for by

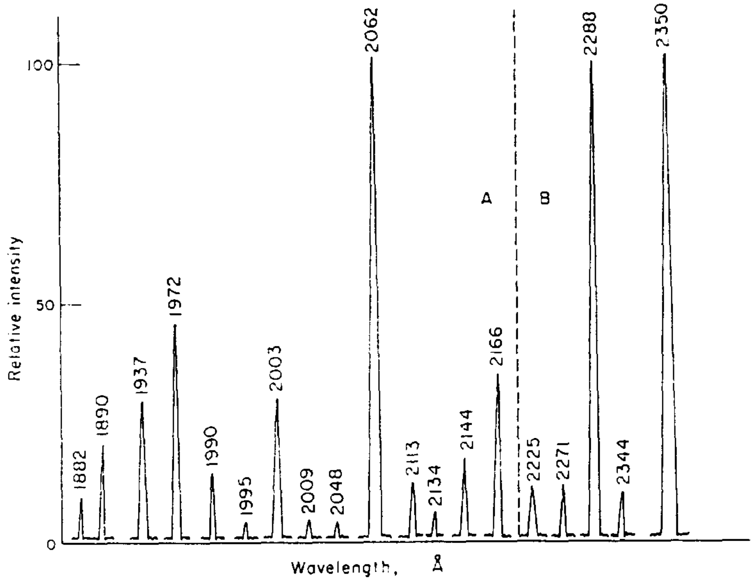

FIG. 1.—Emission spectrum of arsenic discharge tube operated at 30 W.
A—slit 0·008 mm, gain 3·0
B—slit 0·003 mm, gain 3·0

Brode.[10] Not all of the lines shown by Candler are designated, but by calculating the energy differences between the various states and using Candler's table of ground state term differences, the excited state terms can be postulated. It was assumed that the excited terms are regular, although there is no evidence for this other than the fact that the equivalent terms are shown as regular for antimony. Our designations are, however, substantiated by the energy level differences given in the Tables of Spectral Line Intensities.[11] In addition to the arsenic lines the 2062 Å iodine line was quite prominent, but the continuum associated with tubes containing only free iodine was absent.

The tube was best operated at a power rating of 30 W with the upper 2 cm in the cavity and 2 cm protruding below it with a very slight air-draught applied to the bottom of the tube from a compressed air supply. The discharge had a light blue colour under these conditions, but the cavity tuning was found to be rather critical. A spectrum obtained with a Unicam SP 900A spectrophotometer is shown in Fig. 1. A stability plot recorded over a period of 1 hr showed a maximum ±2% variation in response. There were no sudden fluctuations and the variation occurred in the form of gradual drifts.

ATOMIC-FLUORESCENCE MEASUREMENTS

Flames

A $10^{-3}M$ solution (75 ppm) of arsenic (prepared by dilution of a $10^{-2}M$ solution containing 0·989 g of arsenious oxide per l. of distilled water) was nebulized into normal air–acetylene, air–propane and air–hydrogen flames and diffusion flames of nitrogen–hydrogen[8,12] and argon–hydrogen.[8] Under optimised conditions the normal premixed flames all gave similar responses. However, when a $10^{-3}M$ solution of potassium arsenate (prepared by dissolving 0·180 g of potassium arsenate per l. of distilled water) was nebulized, the air–acetylene and air–hydrogen flames gave the better response. This indicates incomplete dissociation of potassium arsenate, especially in the relatively cool diffusion flames. In consequence, both the air–acetylene and the two diffusion flames were studied, using solutions of arsenious oxide. The air–acetylene and the diffusion flames were obtained by using the standard acetylene jet and 1·8 × 7·0 cm acetylene emission head supplied with the Unicam SP

900A spectrophotometer. The steel head of this burner is perforated at one end by a square array of 13 holes.

Wavelength of measurement

Solutions of arsenious oxide were nebulized under optimized conditions into air–acetylene and nitrogen–hydrogen flames. The intensity of the signal was found to be dependent on the type of flame, the line at which the fluorescence was measured and the arsenic concentration. The results obtained at the 1937 Å resonance line are shown in Table I. A similar effect was observed at other resonance and some non-resonance fluorescence lines. At low concentrations (<200 ppm) the nitrogen–hydrogen flame gave the better response, but at high concentrations (>200 ppm) the calibration curves curved towards the concentration axis. The calibration curves for the three resonance lines in the nitrogen–hydrogen flame are shown in Fig. 2 together with the calibration curve obtained at 1972 Å in the air–acetylene flame. It can be seen that in the diffusion flame at low concentrations the 1890 Å resonance line gives the best response followed by the 1937 Å line and then the 1972 Å line. However, at high concentrations the order is reversed and the 1972 Å line gives the best response. As stated previously, the air–acetylene flame gives better linearity and sensitivity at high arsenic concentrations for a given line than the diffusion flame. This can be seen for the 1972 Å line in Fig. 2. The strongly reducing cool diffusion flame contains a higher density of arsenic atoms than the hot air–acetylene flame and this accounts for the higher resonance fluorescence intensities at low arsenic concentrations with the diffusion flame. At high arsenic concentrations this higher density of arsenic atoms causes self-absorption of the emitted resonance radiation. Hence, the diffusion flame calibration line curves more rapidly than that obtained in the air–acetylene flame.

TABLE I.—RELATIVE FLUORESCENCE EMISSION AT 1937 Å

Flame	Relative fluorescence reading	
	As 75 ppm	As 750 ppm
N_2/H_2	35	35*
Air/C_2H_2	22	40

* Reading set to 35 divisions on recorder.

In addition to the resonance emission at 1890, 1937 and 1972 Å, 12 non-resonance fluorescence signals were observed. The relative fluorescence readings are shown for the premixed air–acetylene and nitrogen–hydrogen diffusion flames in Table II, and Fig. 3 shows the fluorescence spectrum obtained in the diffusion flame.

Table II shows that there are striking differences between the relative intensities of various lines in the two flames, probably due to differences in flame absorption at the same wavelength as the exciting resonance lines. Also, because of its greater atomic population there is more absorption of the resonance lines in the diffusion flame than in the air–acetylene flame. However, only measurement at a *resonance* line in the diffusion flame is subject to self-absorption effects of the emitted radiation. If measurement is made at a non-ground state line (direct-line fluorescence), then this radiation will not suffer any self-absorption before leaving the flame. This accounts

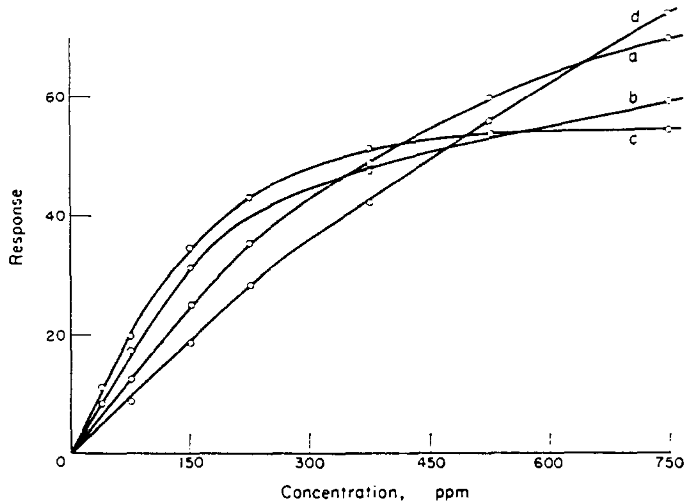

FIG. 2.—Arsenic calibration curves at various wavelengths.
a at 1972 Å in N_2/H_2 diffusion flame, slit 0·325 mm, gain 3·5.
b at 1937 Å in N_2/H_2 diffusion flame, slit 0·325 mm, gain 3·5.
c at 1890 Å in N_2/H_2 diffusion flame, slit 0·325 mm, gain 3·5.
d at 1972 Å in air/C_2H_2 flame slit 0·325 mm, gain 3·5.

for the relative increase in intensity of the direct-line fluorescence signals for the nitrogen–hydrogen flame as compared to those for the air–acetylene flame at high arsenic concentrations.

It was expected that the high rate of curvature of the calibration graphs observed for the resonance fluorescence processes would not be so marked at the corresponding direct-line or thermally-assisted direct-line fluorescence processes. This was found to be so for the fluorescence emission at 2350 Å in both flames. Fluorescence readings at the 1890 Å line, which is the primary absorption line for emission at 2350 Å, give a calibration curve that is parallel to the concentration axis for above 300 ppm of arsenic in the nitrogen–hydrogen flame (*cf.* Fig. 2). However, if measurements are taken at the 2350 Å line, the curve does not become horizontal even at 600 ppm of arsenic. The 2288 Å ($^2P_{1\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}{}^0$), 2350 Å ($^2P_{\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}{}^0$), 2745 Å ($^2P_{1\frac{1}{2}} \rightarrow {}^2P_{\frac{1}{2}})^0$, 2780 Å ($^2P_{1\frac{1}{2}} \rightarrow {}^2P_{1\frac{1}{2}}{}^0$). 2861 Å ($^2P_{\frac{1}{2}} \rightarrow {}^2P_{\frac{1}{2}}{}^0$) and the 2899 Å ($^2P_{\frac{1}{2}} \rightarrow {}^2P_{1\frac{1}{2}}{}^0$) lines are all examples of thermally-assisted direct-line fluorescence which has been previously observed for bismuth[8] and postulated for antimony.[7] The relatively high fluorescence intensity of the 2350 Å line is due to the low energy difference between the $^4P_{2\frac{1}{2}}$ and the $^2P_{\frac{1}{2}}$ states (0·027 eV) and the favoured $^2P_{\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}{}^0$ transition. This transition is spin-allowed, unlike the 2381 Å ($^4P_{2\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}{}^0$) "direct" intercombination line. Arsenic is an atom of fairly low atomic weight that would be expected to give some degree of Russell-Saunders coupling. Hence the relatively high intensity of the 2350 Å line compared with that of the three "direct" intercombination lines. It must be remembered that the $^2P_{\frac{1}{2}}$ state can only be populated from the $^4P_{2\frac{1}{2}}$ state, which in turn can only be populated by absorption of the 1890 Å ($^4P_{2\frac{1}{2}} \rightarrow {}^4S_{1\frac{1}{2}}{}^0$) line, which is not the most sensitive for resonance fluorescence at an arsenic concentration of 750 ppm. The $^2P_{\frac{1}{2}}$ state can not be populated by absorption of the 1882 Å ($^2P_{\frac{1}{2}} \rightarrow {}^4{}_{1\frac{1}{2}}S^0$) intercombination line as this line was found not to be absorbed. This was to be

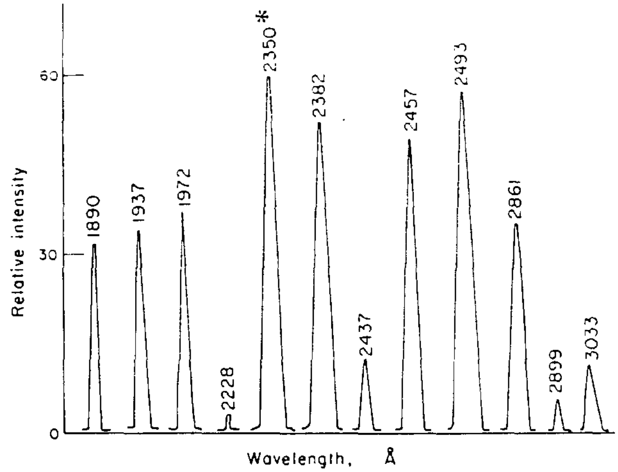

FIG. 3.—Atomic-fluorescence spectrum in nitrogen–hydrogen diffusion flame. Arsenic 750 ppm, slit 0·1 mm, gain 3·0.
Emission signals at 2745 and 2780 Å are too low to be shown.
* Multiply intensity scale by 2 to compare with other emission signals.

TABLE II.—RELATIVE RESONANCE FLUORESCENCE INTENSITIES

Line, Å	Transition	Relative fluorescence signal*	
		Air/C_2H_2	N_2/H_2
1890	${}^4P_{2\frac{1}{2}} \rightarrow {}^4S_{1\frac{1}{2}}{}^0$	26	37
1937	${}^4P_{1\frac{1}{2}} \rightarrow {}^4S_{1\frac{1}{2}}{}^0$	40	40
1972	${}^4P_{\frac{1}{2}} \rightarrow {}^4S_{1\frac{1}{2}}{}^0$	40	43
2288	${}^2P_{1\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}{}^0$	58	4
2350	${}^2P_{\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}{}^0$	168	144
2382	${}^4P_{2\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}{}^0$	33	58
2437	${}^4P_{1\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}{}^0$	9	13
2457	${}^4P_{1\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}{}^0$	45	53
2493	${}^4P_{\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}{}^0$	44	61
2745	${}^2P_{1\frac{1}{2}} \rightarrow {}^2P_{\frac{1}{2}}{}^0$	†	‡
2780	${}^2P_{1\frac{1}{2}} \rightarrow {}^2P_{1\frac{1}{2}}{}^0$	†	‡
2861	${}^2P_{\frac{1}{2}} \rightarrow {}^2P_{\frac{1}{2}}{}^0$	†	40
2899	${}^2P_{\frac{1}{2}} \rightarrow {}^2P_{1\frac{1}{2}}{}^0$	†	6
3033	${}^4P_{1\frac{1}{2}} \rightarrow {}^2P_{1\frac{1}{2}}{}^0$	†	13
3120	${}^4P_{\frac{1}{2}} \rightarrow {}^2P_{1\frac{1}{2}}{}^0$	†	¶

* Scale reading; 750 ppm arsenic solution used with slitwidth 0·1 mm and gain 3·0.
† Air/C_2H_2 flame background too high to permit accurate measurements.
‡ Only observed with wider slitwidths and higher gains.
¶ Measurement uncertain due to proximity of OH band emission.

expected, because the equivalent antimony line at 2127 Å ($^2P_{\frac{1}{2}} \rightarrow {}^4S_{1\frac{1}{2}}{}^0$) is only absorbed very weakly[7] and antimony does not obey the Russell-Saunders coupling rules as closely as arsenic.

The thermally-assisted direct-line fluorescence signals from the $^2P_{1\frac{1}{2}}$ state, which lies 0·21 eV above the $^4P_{2\frac{1}{2}}$ state, were much weaker than those from the $^2P_{\frac{1}{2}}$ state (*cf.* Tables II and III). These fluorescence signals (from the $^2P_{1\frac{1}{2}}$ state) were very weak in the cool diffusion flame, but were stronger in the high temperature air–acetylene flame, as would be expected. The fluorescence at 2288 Å ($^2P_{1\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}{}^0$) was 15 times as strong in the hotter premixed flame (cf. Table II).

TABLE III.—RELATIVE QUENCHING EFFECTS OF NITROGEN AND ARGON

Line, Å	Relative fluorescence intensity*	
	N_2/H_2	A/H_2
1890	32	33
1937	34	46
1972	37	53
2288	3	5
2350	116	208
2382	52	56
2437	12	17
2457	48	67
2493	56	80
2745	<0·5†	~0·5†
2780	0·5†	1·0†
2861	34	63
2899	5	85
3033	11	15
3120	‡	‡

* 750 ppm arsenic solution used with slitwidth 0·1 mm and gain 3·1.

† Observed at wider slitwidths, higher gains.

‡ Measurements uncertain due to proximity of OH band emission.

The relative quenching effects of nitrogen and argon were found by comparing the intensity of the fluorescence signals in the nitrogen–hydrogen and argon–hydrogen diffusion flames. The results shown in Table III indicate that the lines emanating from the $^4P_{2\frac{1}{2}}$ state are unaffected when argon is substituted for nitrogen, whilst those from the $^4P_{1\frac{1}{2}}$ state are increased by *ca* 33%, those from the $^4P_{2\frac{1}{2}}$ state by *ca.* 40% and those from the $^2P_{\frac{1}{2}}$ state by *ca.* 80%. This last figure was considered to be unusual as any atoms in the $^2P_{\frac{1}{2}}$ state must have arrived there *via* a radiationless transition from the $^4P_{2\frac{1}{2}}$ state and the nitrogen molecule would be expected to favour this transfer more than the argon atom. Obviously the nitrogen molecules must quench atoms in the $^2P_{\frac{1}{2}}$ state to a greater extent than they assist the $^4P_{2\frac{1}{2}} \rightarrow {}^2P_{\frac{1}{2}}$ transition.

The effect of varying the source operating power is shown in Table IV. Increase in operating power appears to favour the fluorescence emission at 1972 Å whilst that at 1890 Å is decreased. This must be due to some self-reversal and pressure broadening of the 1890 Å line in the source at increased power. Operating above *ca.* 35 W caused some instability because of an increase in pressure within the tube.

TABLE IV.—EFFECT OF SOURCE POWER ON FLUORESCENCE INTENSITY

Power rating, W	Fluorescence signal*					
	75 ppm As			750 ppm As		
	1890 Å	1937 Å	1972 Å	1890 Å	1937 Å	1972 Å
30	42	35	26	24·5	26·5	29
43	50	46	36	31	34·5	39
55	54	54	43·5	32	37	47

* The fluorescence intensity readings were obtained with a slitwidth of 0·5 mm, and gains 3·0 for 75 ppm As and 3·10 for 750 ppm As. The discharge tube was uncooled.

TABLE V.—SOME LIMITS OF DETECTION* BY ATOMIC-FLUORESCENCE SPECTROSCOPY

Line, Å	N_2/H_2 flame		Air/C_2H_2 flame	
	Limit, ppm	Slitwidth, mm	Limit, ppm	Slitwidth, mm
1890	0·2	2·0	1·0	2·0
1937	0·25	2·0	1·0	1·5
1972	0·5	2·0	2·0	1·5
2350	0·15	2·0	2·0	1·0

* Signal-to-noise ratio = 1.

Calibration curves have been obtained with aqueous solutions of arsenious oxide over the range 5–750 ppm of arsenic at the 1890, 1937 and 1972 Å resonance lines and at the 2350 Å thermally-assisted direct line. In the diffusion flames the 1890 Å line was the most sensitive resonance line at low concentrations, but suffered serious curvature towards the concentration axis above 150 ppm of arsenic. The 1972 Å line was the most sensitive resonance line at high concentrations of arsenic, and gave more nearly linear calibration curves. The 1937 Å line was intermediate in behaviour as expected. The air–acetylene flame gave similar results except that the 1937 Å line gave greater sensitivity at low concentrations of arsenic, possibly because the strong flame absorption at 1890 Å resulted in a high signal:noise ratio. The 2350 Å thermally-assisted direct-line fluorescence signal was the most sensitive, but the increased background of the air–acetylene flame was sufficient almost to offset the increased sensitivity. It was also found that the air–acetylene flame gave straighter calibration curves over a given concentration range of arsenic at a given line than the diffusion flames did. At low arsenic concentrations the nitrogen–hydrogen flame was more sensitive and for high concentrations (*ca.* 500 ppm) the air–acetylene flame was the more sensitive. This is probably because of the higher density of arsenic atoms in the more strongly reducing cooler flame, which causes self-absorption of the emitted radiation at high arsenic concentrations. The limits of detection in aqueous solution are shown in Table V for the main arsenic lines. Prior extraction of arsenic into organic solvents should considerably increase these limits[12] as also would source modulation. The limit of detection at 2350 Å is 0·2 ppm, when using a low background air–hydrogen flame, which like the air–acetylene flame is hot enough to give complete breakdown of all arsenic species. The limits of detection shown in Table V at the three resonance lines are especially good when it is realized that the photomultiplier used in these studies (EMI 9601 B) has a Corning glass window and has virtually no response below *ca.* 2000 Å.

A filter interposed between the source and the flame so as to transmit radiation at 1890 Å, and another filter between the diffusion flame and the photomultiplier to transmit radiation at 2350 Å,[13] should lead to considerably better sensitivity limits. The diffusion flame has no background at 2350 Å and this arrangement would overcome the large light losses which occur in the monochromator and also any scattering that might be observed at low arsenic concentrations. According to Jenkins and White[14] a thin film of sodium metal on quartz is opaque to all wavelengths except those near 1950 Å.

With the premixed air–acetylene flame, the only interferences observed from a wide range of elements were due to intense light emission from easily excited elements such as Na, K, Cu, reaching the photomultiplier *via* a light leakage in the monochromator. Source modulation should also overcome this type of interference, which is not peculiar to atomic-fluorescence.

With the diffusion flames described above, interference was observed with 10-fold molar excesses of various cations in a 75 ppm solution ($10^{-3}M$) of arsenic. Up to a 10% decrease in the fluorescence intensity was found with Al^{3+}, Cu^{2+}, Mg^{2+}, Zn^{2+}, Na^+ and NH_4^+ (in decreasing order of interference). Anions such as chloride, nitrate, phosphate and sulphate had little effect. The decreases are considered to be due to the incomplete dissociation of the metal arsenite in the relatively cool diffusion flame. Passing the solutions through a cation-exchange column or even burning the diffusion flame in an oxygen-sheathed atmosphere to increase its temperature should overcome these matrix effects.

ATOMIC-ABSORPTION MEASUREMENTS

The following flames were studied: air–acetylene, air–propane, air–hydrogen, nitrogen–hydrogen–nitrous oxide and nitrogen–hydrogen. Similar results to those quoted by Slavin *et al.*[3] were obtained with the first three flames. Transmission signals of 18, 33·5 and 40% were obtained at 1890, 1937 and 1972 Å respectively with a 7·0-cm burner. The flame absorbance for the air–acetylene flame was very dependent on flame conditions and reached a minimum for a flame on the verge of luminosity. It was at this point, which also corresponds to the point of maximum absorbance by the arsenic atoms, that the measurements were made. The opacity of the nitrogen–hydrogen–nitrous oxide flame below 2000 Å renders it inferior to the air–acetylene flame and it was not, therefore, used. The 7-cm nitrogen–hydrogen diffusion flame burning on a 7-cm perforated propane burner plate showed little flame absorption at any wavelength. The flame absorption was also not very dependent on the hydrogen pressure, and transmission figures of 70, 87 and 95% were obtained at 1890, 1937 and 1972 Å respectively. If a slot-burner with less air entrainment were used, even higher transmission figures should be obtained. Flame absorption with the air–acetylene flame was maximal when the burner head was level with the monochromator slit, but was minimal for the nitrogen–hydrogen flame. This shows that flame absorption is at a minimum along the centre of the diffusion flame, which contains mainly non-absorbing nitrogen and hydrogen. Towards the edges of the flame air entrainment takes place, thus causing increased light absorption. This can be illustrated by slightly altering the burner position. Best results were obtained with the burner-head

Table VI.—Atomic-absorption measurements with an electrodeless discharge tube

Line, Å	Absorbance for 75 ppm As	
	N_2/H_2	Air/C_2H_2
1882	0·000	0·000*
1890	0·398	0·118
1937	0·332	0·092
1972	0·200	0·055

* Zero absorbance was also given with 750 ppm of arsenic.

level with the bottom of the monochromator slit for the air–acetylene flame and *ca.* 2 mm above it for the nitrogen–hydrogen flame. Table VI shows the absorbance measurements obtained at the four resonance lines on nebulizing a 75 ppm solution of arsenious oxide into these two flames. The arsenic electrodeless discharge tube was used as source and was placed in the usual position, but slightly out of focus to prevent too much light from reaching the detector.

Metal arsenite solutions gave higher absorbance readings in the air–acetylene flame than in the diffusion flame, thus indicating incomplete dissociation in the latter flame. This can presumably also be overcome by first passing the solutions through a cation-exchange column.

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Zusammenfassung—Es wird die Konstruktion einer elektrodenlosen Arsen-Entladungsröhre und ihre Verwendung zu Atomfluoreszenzuntersuchungen beschrieben. Kühle Stickstoff-Wasserstoff- und Argon-Wasserstoff-Diffusionsflammen sowie auch normale vorgemischte Flammen werden als Atomreservoirs in Betracht gezogen und die Atomfluoreszenzemission bei 15 verschiedenen Wellenlängen ermittelt. Die Diffusionsflammen geben bei Arsenkonzentrationen unter 200 ppm die größten Emissionssignale, biegen aber bei hßheren Konzentrationen wegen der abnormal großen Dichte an Arsenatomen vorzeitig um. Über 200 ppm Arsen ist die vorgemischte Luft-Acetylen-Flamme besser. Die Nachweisgrenze bei 1890 Å beträgt 0,2 ppm Arsen in der Stickstoff-Wasserstoff-Diffusionsflamme und 1,0 ppm in der Luft-Acetylen-Flamme. Eine Diffusionsflamme großer Schichtdicke ist auch bei Atomabsorptionsmessungen besonders nützlich, da sie im fernen Ultraviolett sehr wenig Strahlung absorbiert und eine große Menge Arsenatome liefert.

Résumé—On décrit la construction d'un tube à décharge d'arsenic sans électrode et son emploi pour des études de fluorescence atomique. Des flammes de diffusion froides d'azote-hydrogène et argon-hydrogène ainsi que des flammes normales pré-mélangées sont considérées comme des réservoirs d'atomes et on évalue l'émission de fluorescence atomique à 15 longueurs d'onde différentes. Les flammes de diffusion donnent les signaux d'émission les plus importants à des concentrations en arsenic inférieures à 200 p.p.m., mais montrent une courbure précoce aux concentrations plus élevées à cause de la présence d'une densité anormalement élevée d'atomes d'arsenic. Au-dessus de 200 p.p.m. d'arsenic, la flamme pré-mélangée air-acétylène est supérieure. La limite de détection à 1890 Å est de 0,2 p.p.m. d'arsenic dans

la flamme de diffusion azote-hydrogène et de 1,0 p.p.m. dans la flamme air-acétylène. Une flamme de diffusion à long parcours est également particulièrement utile dans les mesures d'absorption atomique parce qu'elle absorbe très peu de radiations dans la région ultra-violette olintaine et donne une abondance d'atomes d'arsenic.

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A NEW CONCEPT OF AUTOMATED RADIOCHEMICAL ANALYSIS BASED ON SUBSTOICHIOMETRIC SEPARATION

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Summary—Tracer methods, such as radioisotope dilution, radiometric analysis, concentration dependent distribution, saturation analysis *etc.*, are compared on a basis of radioactivity–mass balance relationships, and their automation is proposed. The requirements of a chemical separation, which is an integral part of these methods, are discussed. It is shown that automation, in addition to its obvious advantages, enables entirely new procedures to be developed, based on chemical separations which do not give reproducible results when performed normally. Simple commercially available apparatus has been used to verify these concepts by determination of traces of mercury. As little as 0·005 ppm of Hg can be determined, the detection limit being about a tenth of this. In the range 2·4–0·03 ppm, 20 samples/hr can be analysed, for lower amounts the sampling rate is 10 samples/hr.

TRACER methods are enjoying a small renaissance in the field of radiochemical analysis. There is a need for simple and sufficiently sensitive analytical methods and many radiochemists seem to be more and more reluctant to use the destructive activation-analysis which, in addition to its excellent qualities also has some well-known drawbacks. Therefore, substoichiometric isotope dilution,[1,2] concentration dependent distribution,[3–6] saturation analysis[7,8] and quantitative isotope dilution-methods[9,10] have been developed because they require much less complicated (and expensive) instrumentation than activation-analysis and are still potentially at least as sensitive. Usually, however, the simpler the instrumentation the more sophisticated is the chemistry involved. The chemical separation methods applied must permit separation of submicrogram quantities of elements with the same degree of reproducibility as for milligram quantities. If that is not the case, both the precision and reproducibility of the determinations are affected, because the activities are measured on the separated material. This can be seen from the radioactivity–mass balance relationship

$$yS = (x + y)S_x \tag{1}$$

where $S = A/m$, $S_x = A_x/m_x$ are the specific activities before and after isotopic dilution of the quantity, y, of a radiotracer with the quantity, x, of non-active form of the same element. A and A_x are the activities of the *separated* amounts m and m_x of the element before and after mixing of active and non-active isotopes has taken place. Therefore

$$yA\frac{m_x}{m} = (x + y)A_x \tag{2}$$

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and for analytical purposes, x should be measured through a change of A_x. For this purpose the rest of the variables in (2) must be known (and preferably be kept constant for automation) within the working range of x. However, this is most difficult to achieve for the ratio m_x/m. Clearly a *quantitative* separation is useless as $m = y$ and $m_x = x + y$. If *substoichiometric* separation is used (which ensures constant yield of the test element), then $m_x/m = 1$ and

$$x = y\left(\frac{A}{A_x} - 1\right). \tag{3}$$

The constant yield of test element is achieved through choice of the conditions (pH, *etc.*) so that a suitable chelating agent (dithizone, diethyldithiocarbamate, cupferron, EDTA *etc.*), added in substoichiometric quantity, is completely consumed by formation of a chelate which is subsequently separated by solvent extraction or by ion-exchange. If the value of m_x/m increases less than 1% for a tenfold increase of x then equation 3 is still valid for practical purposes and substoichiometric *radioisotope dilution* can be carried out. However, this requirement to a certain extent limits the choice of a suitable reagent to those which react fast enough and forms complexes with high stability constants.[1–6]

For $m_x \neq m$, equation (2) changes to

$$x = m_x \frac{A_t}{A_x} - y \tag{4}$$

where $A_t = S \cdot y$, the total activity added. As shown below, this equation applies for a whole range of methods.

In the method of *radiometric microanalysis* due to Ehrenberg[11] the amount of reagent used is stoichiometrically equivalent to y. Therefore $m_x = y$ and consequently $x = m_x(A_t - A_x)/A_x$. Here the ratio m_x/m remains constant, but may be bigger than 1. If, for chemical reasons, $m_x/m \neq$ constant, a calibration graph must be used. Thus *concentration dependent distribution methods*[3–6] have been developed by De Voe *et al.* and also by Kyrš. By keeping y and A_t constant, m_x/A_x is found experimentally for different x-values. The calibration graph is obtained either as $x = f(A_x)_{y,A_t}$ or $x = f(A_t/A_x)_{y,A_t}$. This approach has the usual advantages and disadvantages of methods which rely on a calibration curve. *Saturation analysis*[7,8] (*radioimmunoassay*) is similarly based on the use of a calibration graph of $x = f[(A_t - A_x)/A_x]_{y,A_t}$. Finally, Suzuki's *quantitative isotope dilution*[9,10] must be mentioned, as it is basically the same.

It is a matter of opinion which name should be used for this group of methods, but the principle on which they are based is the same in all cases. Briefly, substoichiometric radioisotope dilution [equation (3)] is based on measurement of the *change of specific activity* when the separation yield is kept constant. All radiometric methods [equation (4)] are based on the measurement of the *change of distribution of radioactive species* between two phases caused by presence of a non-active species. It is shown below that this definition not only serves as a classification, but also has practical implications.

These methods, although they differ in principle, are all based on substoichiometric separation and can therefore be automated on the same basis. Two methods are possible: in the fully automated method radioactivity is introduced continuously, and in the semi-automated method radioactivity, being present in each sample, is fed into the machine discontinuously.

Fully automated method. A solution of original specific activity S is continuously fed into a machine (Fig. 1a) at a rate y. After substoichiometric separation, the activity A of fraction m is continuously measured and registered (baseline). By introducing increasing amounts of x, the calibration graph is obtained. The greater x is, the larger becomes the depression of activity (A_x) registered as a "negative" peak. It should be noted that apart from the shape of the calibration curve, there is no difference between substoichiometric isotope dilution ($m_x/m = 1$) and radiometric methods [$m_x/m = f(x)$, dotted line] in this case, for both S and A_t are automatically kept constant over the whole range of x-values.

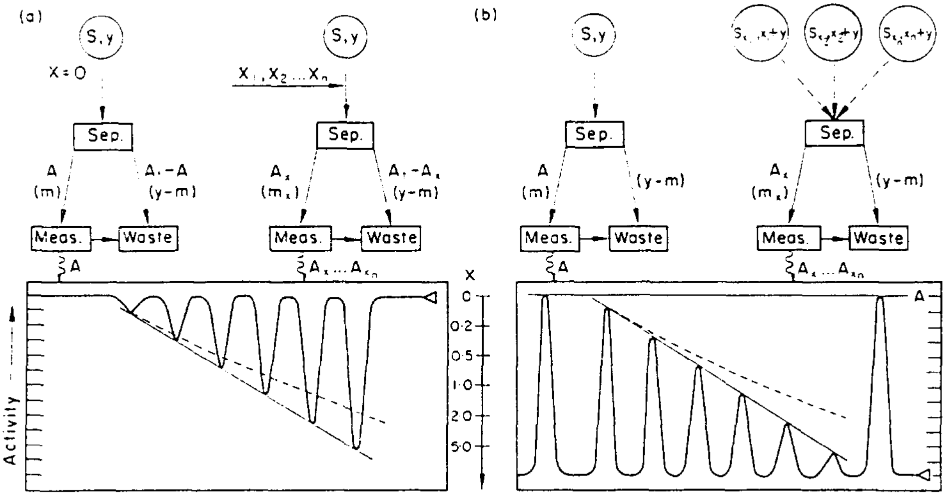

FIG. 1.—Concept of automated radiochemical analysis.

Semi-automated method. This involves some pretreatment of the test sample (destruction, preliminary concentration *etc.*) before it is fed into the machine, to be further processed automatically. Radioisotope can either be mixed in the machine with the pretreated sample as indicated in Fig. 1a, or, better, added manually to the sample before pretreatment (Fig. 1b). The latter approach is preferable as any losses of the species to be determined, which may occur during dissolution or preliminary separation, will not influence the analytical result. As the original specific activity S decreases to a value S_x, because of the presence of x, the calibration graph is obtained by measuring and registering the activities A and A_x as a function of the separated quantities m and m_x. Line A, which is proportional to the original specific activity of $y(x = 0)$, serves as a baseline for x. The higher x is, the lower is the peak. The shape of the calibration graph obtained can be described either by equation (3) of (4).

If $m_x/m = 1$, equation (3) is obeyed and the slope of the calibration graph corresponds to the scale as given in Fig. 1. Moreover, any irreproducible losses (up to the value $y - m$) of the species to be determined have no influence on the results.

If $m_x \neq m$, the slope of a calibration graph (dotted line) will be different, simply because $m_x = f(x)$. No losses of material may occur as follows also from equation

(4) which involves *total original* activity A_t. In a practical case an increase of the ratio m_x/m over a range of x must be investigated (*cf.* Fig. 4) and compared with other experimental errors and required precision.

In an earlier paper[12] an experimental method for the determination of mercury by fully automatic substoichiometric isotope dilution has been given. However, it is evident that this approach is also applicable for a whole range of radiometric methods, so in order to verify the idea of a semi-automated method on the same basis, the following experiments on the determination of mercury were carried out.

EXPERIMENTAL

Reagents

All reagents were prepared from analytical grade reagents, unless otherwise stated.

Water. Twice distilled from Pyrex apparatus.

Carbon tetrachloride. Merck, *p.a.*

Hydrochloric acid. Merck, Suprapur.

Radioisotope, ^{203}Hg. Supplied as nitrate in 1*M* nitric acid, original specific activity 300 mC/g (Danish AECE, Risø).

Radioactive mercury solution. About 20 μl of the ^{203}Hg solution are diluted with 0·5*M* hydrochloric acid to 100 ml. This stock solution is diluted to the concentration required for the range of the calibration graph. The mercury content (y) of this solution is checked by reversed isotope dilution.

Inactive mercury solution, $5 \times 10^{-4}M$ *in* 0·1*M hydrochloric acid.* Prepared from weighed amount of mercury(II) chloride. Further diluted to the required concentration with 0·03*M* hydrochloric acid.

Stock dithizone solution, $4 \times 10^{-4}M$ *in carbon tetrachloride.* Prepared from Merck dithizone *p.a.*, and stored in a refrigerator.

Zinc dithizonate stock reagent. Diluted solutions of organic reagents decompose in time and this must be prevented, especially for use in an automated method. In a previous paper,[12] zinc dithizonate was used instead of dithizone, but still further improvement of its stability was observed to be necessary. This was finally achieved in the present work, as follows. Place 2 g of ascorbic acid in a 1-l. Pyrex glass separatory-funnel, dissolve it in *ca.* 25 ml of water, then add 150 ml of 1*M* acetic acid and 150 ml of 1*M* sodium acetate. Extract this solution for a short time with 25 ml of 20-fold diluted dithizone stock solution and discard the separated organic phase. Add 10 ml of 0·1*M* zinc chloride, check the pH and if necessary readjust it to 4·5. Then add *ca.* 300 ml of the 20-fold diluted dithizone stock solution and extract for about 2 min. Separate the organic phase, and filter and store it in a refrigerator. The prepared solution ($1 \times 10^{-5}M$ $Zn(HDz)_2$ in CCl_4) is stable for at least one month. When further diluted 10-fold, it can be used for at least 10 days; $10^{-7}M$ $Zn(HDz)_2$ is stable for at least 2 days and even $5 \times 10^{-8}M$ $Zn(HDz)_2$ can be used when stored under a displacement solution in a displacement bottle (see Fig. 3). It was found that all the solutions must be stored protected from light, in colourless bottles with ground stoppers (a-20, Schott and Gen, Mainz). Dark brown glass bottles, which are generally used for this purpose, must be avoided, as zinc dithizonate rapidly decomposes in contact with this type of glass (which contains large quantities of metals).

Displacement solution. The aqueous phase left over from the zinc dithizonate preparation is separated, filtered and stored in a refrigerator. After 10-fold dilution with water it is used as displacement solution (Fig. 3).

Buffer solution. Dissolve 20 g of acetic acid in water, add 50 ml of 0·1*M* EDTA and 100 ml of 1*M* sodium hydroxide. Dilute to 1 l. and adjust the pH to 3·4. Purify this solution by extraction with two 25-ml portions of 20-fold diluted dithizone stock solution, then wash it with carbon tetrachloride and filter it.

Apparatus

Technicon Auto Analyzer. Sampler II, two-speed proportioning pump, strip-chart recorder (Elliot Dynamaster, Model 570, single point) as supplied by Technicon.

Scintillation counter. A Friesecke and Hoepfner model (West Germany) with a well-type NaI(Tl) crystal, 55 × 55 mm, well-diameter 18 mm, depth 38 mm, was associated with the same manufacturer's ratemeter model FH 57B. The output of this ratemeter (20 V, 3–8 kΩ) is fed into the recorder through a simple adapter consisting of a few resistors and a reference battery (circuit diagram available on request), to give agreement between the scales of the ratemeter and of the recorder, both scales being linear. Change the zero and full scale deflection is less than 0·5% in 8 hr.

Flow-cell. Made of 3·5-mm outside diameter glass tubing. Its construction and function are seen from Fig. 2. The mixture of air and aqueous and organic phases enters the separation trap (A), the separated organic layer is segmented by non-active aqueous solution (B) and then its activity is measured as it passes through a coil placed in the well of the scintillation crystal. The outlet (C) goes to waste (see Fig. 3). This cell has a better resolution than that used in a previous work,[11] as mixing of the organic layer is prevented by the aqueous segmentation. Further, no adsorption of radiomercury on glass (which increases the background) was observed after 3 months of operation, because the aqueous phase (0·1*M* hydrochloric acid–0·5*M* acetic acid) decontaminates the cell continuously. The "effective volume" of this cell can be simply adjusted by a proper choice of the volume of organic phase pumped in at (A) and out at (C) and by the volume of the wash solution (B).

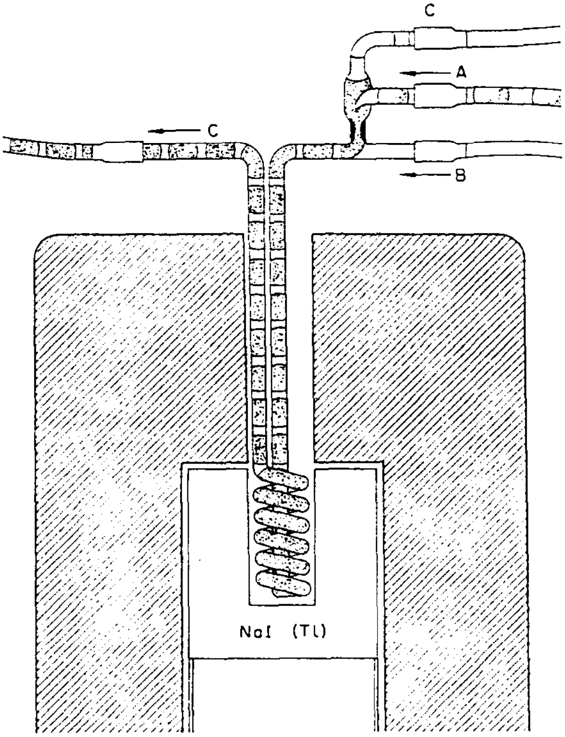

FIG. 2.—Flow cell for measuring radioactivity with NaI(Tl) scintillation detector. Radioactive organic layer is separated from air-bubbles and aqueous phase, segmented by non-active aqueous phase (B) and measured in a coil (volume 0·5 ml).

Manifold. This was constructed from standard parts as supplied by Technicon. To minimize absorption problems, adsorption of radiomercury on all tubing materials and sample cups was measured by using ^{203}Hg (Table I). Clearly, polyethylene, glass and standard tubing are most suitable; and there is only a negligible adsorption of mercury on polystyrene cups from 0·03*M* hydrochloric acid. Therefore transmission solvoflex tubing is used only for waste lines, whereas the standard tubing is used for pumping and its length is minimized. The rest of the lines are made of polyethylene and the whole of the manifold between the HO fitting and the flow-cell is made of glass.

Development of the method

The chemical separation, on which this method is based, consists of solvent extraction of mercury as $Hg(HDz)_2$ with carbon tetrachloride from a slightly acid solution containing EDTA. This medium is used to avoid the interference of bismuth. The suitability of this reaction was first checked manually and then it was automated. From Fig. 3 it is seen that the solvent extraction is carried out in standard single mixing coils, as they were found by us to be superior to all other alternatives. For better mixing of the organic phase, simple jet mixers (marked M) are introduced; for the same reason fitting D2 is used. Zinc dithizonate, dissolved in carbon tetrachloride is introduced into the system by means of the displacement bottle, fitted with a two-way

TABLE I.—ADSORPTION OF RADIOMERCURY ON VARIOUS MATERIALS

Medium	$0{\cdot}03M$ HCl		$1M$ HCl*		pH 3·5, EDTA	
Original content of Hg in solution	cpm 53205	% 100	cpm 0	% 0	cpm 60100	% 100
Material†						
Glass	8210	11·5	1870	3·4	5720	9·5
Acidiflex	12415	23·5	5645	10·7	3498	5·8
Solvaflex	35028	66·0	32024	60·5	54989	91·5
Standard	9151	17·1	6138	11·5	6350	10·5
Polyethylene	795	1·5	—	—	532	0·8

Polystyrene cups.‡

Time	0	30 min	60 min	120 min	300 min	1 day	2 days	4 days	5 days	7 days
% of Hg absorbed	0·16	0·28	0·34	0·43	0·50	0·82	0·66	1·18	1·10	1·14

* Desorption of mercury from previously contaminated material (for 24 hours).

† Activity of 2 cm² of each material after 24 h of contact with 0·2 μg Hg in 2 ml of activity 60·000 cpm.

‡ One millilitre of radiomercury solution containing 0·1 μg Hg in $0{\cdot}03N$ HCl was stored in a 2·0-ml sampler cup for the indicated period. The activities of empty cups were then measured by a well-type scintillation counter and % of Hg adsorbed calculated.

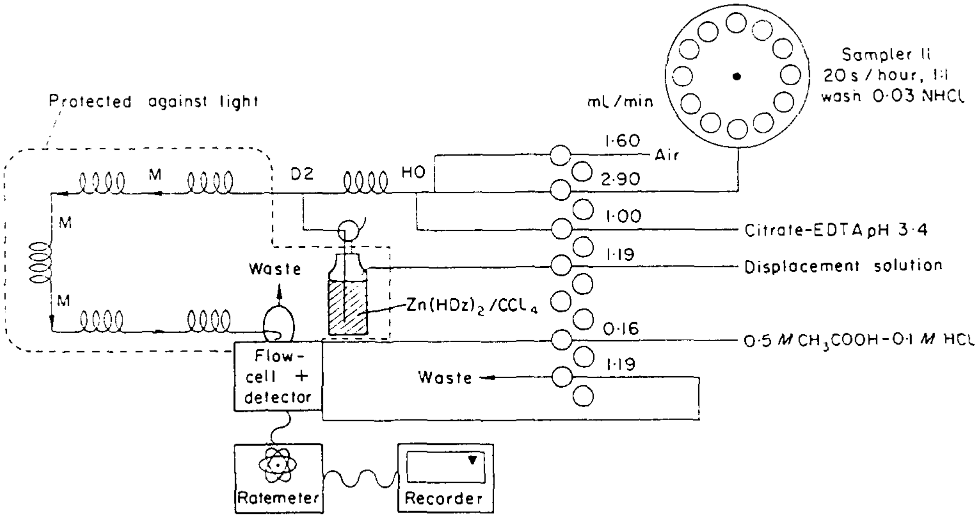

FIG. 3.—Semi-automated method for substoichiometric determination of traces of mercury (manifold).
M—jet mixers. Other symbols according to Technicon.

Teflon stopper. Thus organic phase is protected by a layer of displacement solution and is consequently not in contact with the pumping tubes.

Reproducibility curve. This was investigated with the setting as given in Fig. 3, using $8{\cdot}4 \times 10^{-7}M$ zinc dithizonate in carbon tetrachloride. The resulting graph (Fig. 4) was obtained by plotting the height of the registered peak *vs*. the quantities of mercury (0·012–0·60 μg/ml) present in the sampler cups. The same experiment was repeated with the citrate buffer replaced by $1N$ sulphuric acid. From the shape of the reproducibility curve and from the delivery rates of the reacting solutions (Fig. 3) it follows that Hg(HDz)$_2$ is formed and extracted.

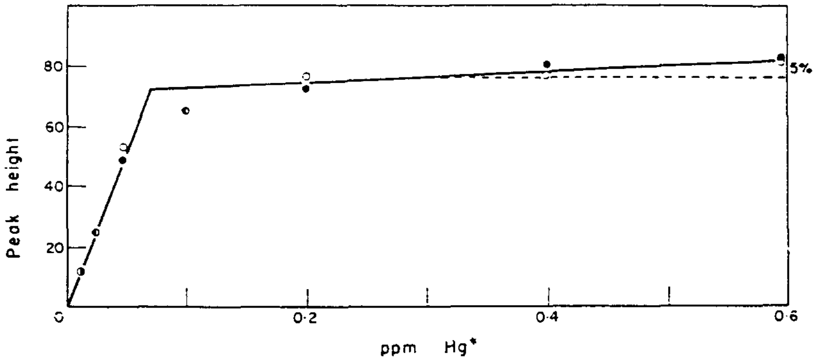

FIG. 4.—Automated substoichiometric separation of mercury.
●—1N H_2SO_4, ○—citrate-EDTA, pH 3·4.

Calibration graph. A series of eleven solutions was prepared by mixing 5·0 ml of radioactive mercury solution (containing 0·5 μg of Hg/ml in 0·03M hydrochloric acid) with the same volume of inactive mercury solution containing respectively 0, 0, 0·03, 0·06, 0·15, 0·30, 0·60, 1·20, 2·40, 0 and 0 μg of Hg/ml in 0·03M hydrochloric acid. These solutions were divided into two halves, one being analysed immediately (Fig. 5, upper right) and the second after 1 : 1 dilution with 0·03M hydrochloric acid (Fig. 5, upper left). The concentration of the zinc dithizonate solution used was 8·4 × $10^{-7}M$ and the experimental arrangement was as indicated in Fig. 3. Thus two calibration graphs were obtained for the initial 0·03–2·4 ppm mercury range, one representing 100% recovery of mercury from an analysed material, and the second only 50% recovery.

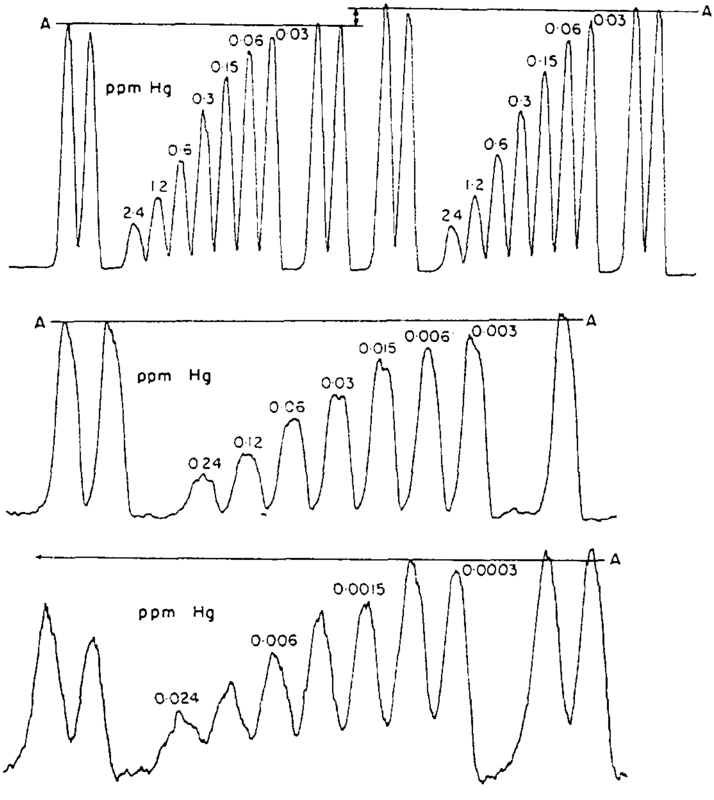

FIG. 5.—Calibration graph for automated substoichiometric determination of mercury.
A is the baseline for zero content of inactive mercury.

For lower concentrations—0·003–0·24 ppm and 0·0003–0·024 ppm—calibration graphs were prepared in the same manner, but the sampling rate was decreased to 10 samples/hr. Only 50% recoveries are presented here (Fig. 5, middle and bottom) as 100% recovery is not likely to be achieved at such low concentrations. For the 0·003–0·24 ppm range 8·4 × $10^{-8}M$ zinc dithizonate was used and 1 × $10^{-8}M$ for the 0·0003–0·024 ppm range, both displacement and return delivery rates being 0·64 ml/min only in the latter case.

RESULTS AND DISCUSSION

From Fig. 4 it can be seen that the amount of extracted mercury is independent of acidity in solutions ranging from pH 3·4 to 1*N* sulphuric acid. Further, the yield of this substoichiometric separation is not strictly constant, as the value of m_x/m increases by about 5% in the range 0·3–0·6 ppm of mercury. The same slope of the reproducibility curve was also obtained for 0·03 ppm and 0·003 ppm of mercury. For the same reason, the standard peaks (line A in Fig. 5) for 100% and 50% recovery differ by about 5%. This deviation, however, can be tolerated when as little as 10^{-3}–10^{-1} ppm of mercury is determined. Further, although quantitative recovery of mercury at this level cannot usually be achieved, recoveries as high as 70–80% are still likely. Therefore, if the standard curve for 100% recovery is used for an actual sample, the reading will be only slightly higher than the true one. The most probable reason why strictly constant yields cannot be obtained is that HgClHDz is formed to some extent from $Hg(HDz)_2$ in the presence of a large excess of mercury.[12,13] Also, extraction may not be complete in the AutoAnalyzer. Further experiments with other elements will surely solve this question.

The sensitivity of this method for mercury is limited by two factors, which are evident from the calibration graph for 0·0003–0·024 ppm of mercury (Fig. 5, bottom). First, due to the low activity measured in this case, both baseline and peaks are not well defined in spite of the fact that a rather long integration time (60 sec) was used. Next, 1 × $10^{-8}M$ zinc dithizonate is not stable enough and therefore the standard level (A) decreases with time (the arrow indicates the level which should be reached by the last two standard peaks). If there is a need for determination of mercury at this very low level, this might probably be achieved by use of a higher specific activity than that used in this work. (This particular graph was obtained by using a ^{203}Hg sample with specific activity ~100 mC/g of mercury, but 1000 mC/g mercury is now commercially available.) Further stabilization of "standard level" A at this dilution is probably achievable by combination of two techniques: use of a displacement bottle and zinc dithizonate prepared as described above, and dilution *in situ* as proposed previously.[12]

Adsorption problems are now solved completely by a choice of construction materials and of reaction medium, and by devising a new cell and the simplest possible manifold. Thus good resolution and a stable baseline are obtained and "carry-over" is minimized as can also be seen from Fig. 5.

CONCLUSION

A new concept of automated radiochemical analysis based on substoichiometric separation is proposed and has been experimentally verified. It has been shown that in a semi-automated method the radiotracer should always be added manually in the same quantity at the start of the procedure. This approach has two advantages: losses of species to be determined are automatically corrected and the amount of radioactivity consumed is less than half of that necessary for the fully automated method.

To apply the present findings to practical analysis, work is in progress to develop a sensitive method for determination of mercury in various biological materials. It is believed that a semi-automated procedure involving the destruction method devised by the British Analytical Methods Committee[14] and automated substoichiometry will serve this purpose.

Acknowledgement—We are indebted to Mr. Lars Mikkelsen for skilled glass-blowing. The automated instrumentation was placed at our disposal through a grant given by The Carlsberg Foundation, to which we express our gratitude.

Zusammenfassung—Tracermethoden wie Verdünnung mit Radioisotopen, radiometrische Analyse, konzentrationsabhängige Verteilung, Sättigungsanalyse usw. werden auf Grund von Beziehungen zwischen Radioaktivität und Masse verglichen und ihre Automation vorgeschlagen. Die Erfordernisse einer chemischen Abtrennung, die einem unbedingt notwendigen Teil dieser Methoden darstellt, werden diskutiert. Es wird gezeigt, daß die Automation zusätzlich zu ihren offenkundigen Vorteilen die Entwicklung ganz neuer Arbeitsvorschriften gestattet, die auf bei normaler Ausführung nicht reproduzierbaren chemischen Abtrennungen beruhen. Einfache, im Handel erhältliche Geräte wurden verwendet, um an der Bestimmung von Quecksilberspuren diese Gedankengänge zu verifizieren. Es können 0,005 ppm Hg bestimmt werden, die Nachweisgrenze beträgt etwa ein Zehntel davon. Im Bereich von 2,4 bis 0,03 ppm können 20 Proben pro Stunde analysiert werden, bei Kleineren Mengen 10 Proben pro Stunde.

Résumé—Les méthodes aux traceurs, comme la dilution radioisotopique, l'analyse radiométrique, le partage dépendant de la concentration, l'analyse de saturation, etc., sont comparés sur la base de relations radioactivité-équilibre de masse, et l'on propose leur automation. On discute des conditions nécessaires à une séparation chimique, qui est une partie intégrante de ces méthodes. On montre que l'automation, en plus de ses avantages évidents, rend possible le développement de techniques entièrement nouvelles, basées sur des séparations chimiques qui ne donnent pas des résultats reproductibles lorsqu'elles sont réalisées normalement. On a utlisé un appareil simple et commercialement accessible pour vérifier ces concepts par la détermination de traces de mercure. On peut doser une quantité aussi faible que 0,005 p.p.m. de Hg, la limite de détection étant d'environ le dixième de cette valeur. Dans le domaine 2,4–0,03 p.p.m., on peut analyser 20 échantillons par heure, pour des quantités plus faibles, la cadence est de 10 échantillons/heure.

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SHORT COMMUNICATIONS

Determination of organic bases in non-aqueous solvents by catalytic thermometric titration

(*Received* 21 *September* 1967. *Accepted* 19 *January* 1968)

IN PREVIOUS papers[1–3] we described the principles of catalytic thermometric titration of some organic bases in acetic acid solution. The method for the determination of tertiary amines and salts of organic acids in acetic acid is based on titration with standard perchloric acid solution in the presence of 2% of water and 8% of acetic anhydride. After the equivalence point, the excess of perchloric acid catalyses the exothermic indicator reaction of water with acetic anhydride. The end-point was determined from the graph of temperature against volume of added titrant or by means of a calibration curve. In the catalytic thermometric titrations described, the standard solution was added discontinuously, while the temperature changes were measured either with a thermometer or a thermistor. During the titration it was necessary to read the chronometer and temperature or the galvanometer as fast as possible and immediately make a further addition of the titrant.

In the present work, the temperature was measured by means of a thermistor connected in circuit with a recorder, which enabled us to read the temperature continuously, increase the accuracy of the determination and generally simplify the titration. In addition, we have carried out titrations by continuously adding the standard solution by means of an automatic piston burette. With this technique the titration end-point is determined from the intersection of the plot of temperature against time or volume, on semi-log paper. The purpose of this work was also to investigate the possibility of determining weak bases by catalytic thermometric titration, which cannot be achieved in acetic acid.[3] According to Fritz and Fulde, very weak bases can be determined potentiometrically in nitromethane, and Wimer,[5] when studying the effect of the ratio of acetic acid and acetic anhydride in the mixture, noticed that with increase of the latter there was an increase in the potential jump near the equivalence point. We attempted several determinations with the solvents mentioned. The determination of antipyrine, a rather weak base, by catalytic thermometric titration in nitromethane and acetic anhydride, confirmed the dominant role of the dielectric constant of the solvent. By varying the ratio of acetic acid and acetic anhydride, we established that an increase in the concentration of the latter resulted in greater temperature changes at the end-point of the catalytic thermometric titration, and therefore in results of higher precision. This offered the possibility of developing a modification of the catalytic thermometric titration of bases, by generating hydrogen ions coulometrically according to Mather and Anson's method.[7]

EXPERIMENTAL

Titrations in acetic acid

As solvent we used glacial acetic acid (C. Erba, s.g. 1·051), containing less than 0·04% of water.[6] Other chemicals, solutions and apparatus used, as well as the conditions of work, were described in the preceding paper.[2] For temperature reading we used the recorder of a Radiometer Polarograph PO-3h. The thermistor was connected as shown in Fig. 1. The titration is carried out by adding 0·25*N* perchloric acid in acetic acid continuously by means of an automatic piston burette. The curves obtained by this technique are shown in Fig. 2.

In this procedure we stopped the titration 3–4 min after the sudden rise in temperature. The titration end-point was determined graphically, on the basis of the known chart-speed and by plotting on semi-log paper temperature change *vs.* time as ordinate as shown in Fig. 3. The intersection of the straight line and the curve gave the time taken to reach the end-point and hence (from the rate of delivery of titrant) the volume of standard solution used. With a rate of addition of 0·074 ml/min the best results are obtained under the conditions given in this paper.

From Table I it can be seen that the results obtained by this procedure are in agreement with these of potentiometric titrations or those of catalytic thermometric titrations by discontinuous addition of the standard solution.

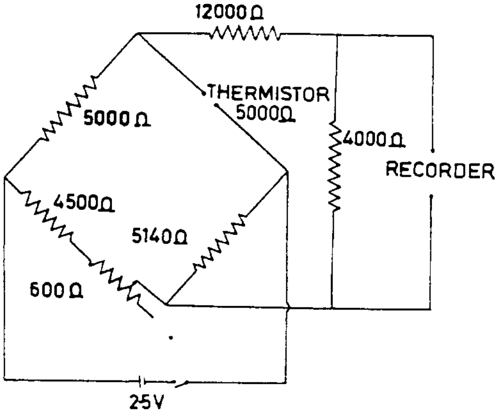

FIG. 1.—Circuit diagram of the thermistor and recorder coupling.

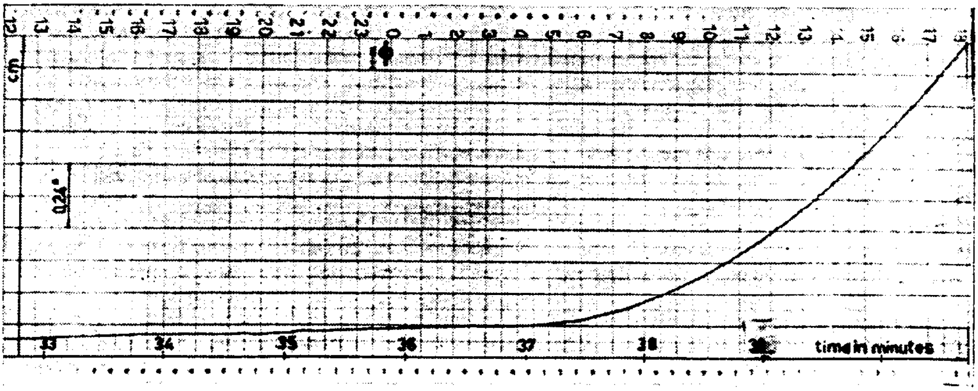

FIG. 2.—Catalytic thermometric titration curve for 2·6 × $10^{-2}M$ solution of potassium acetate in acetic acid obtained by continuous addition of 0·25*M* perchloric acid.

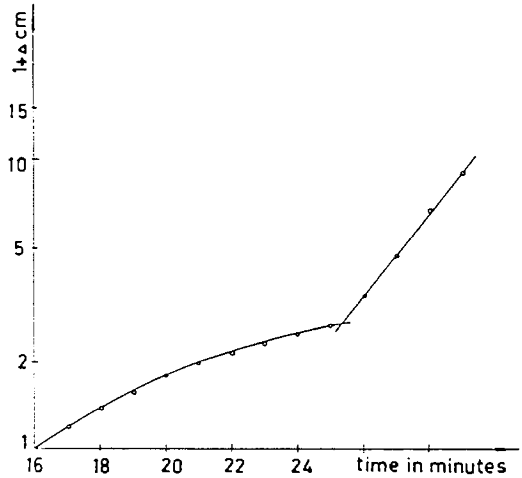

FIG. 3.—Catalytic thermometric titration curve for diethylaniline in acetic acid on continuous addition of 0·25*M* perchloric acid (semi-log paper).

TABLE I.—COMPARISON OF RESULTS OBTAINED BY POTENTIOMETRIC AND CATALYTIC THERMOMETRIC TITRATIONS

Substance titrated	Taken *g*	Potentiometric titration			Catalytic thermometric titration					
					by continuous addition of the titrant			by discontinuous addition of the titrant		
		No. of titrs.	Found, *g*	Average deviation, %	No. of titrs.	Found, *g*	Average deviation %	No. of titrs.	Found, *g*	Average deviation, %
Brucine	0·1500	3	0·1724	1·00	6	0·1713	0·93	3	0·1718	0·18
Diethylaniline	0·0500	3	0·0480	0·07	6	0·0481	0·28	3	0·0490	0·26
Potassium acetate	0·0500	6	0·0473	0·56	4	0·0474	0·50	6	0·0483	0·33
Triethylamine	0·1000	5	0·0962	0·07	4	0·0969	0·31	3	0·0965	0·36

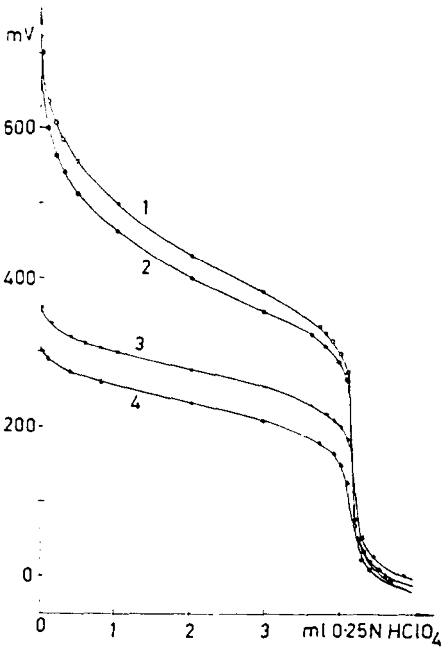

FIG. 4.—Potentiometric titration curves for antipyrine with 0·25*M* perchloric acid in different solvents. 1—in nitromethane with 8% of acetic anhydride present; 2—in acetic anhydride; 3—in acetic acid with 8% of acetic anhydride present; 4—in acetic acid.

TABLE II.—COMPARISON OF RESULTS OBTAINED BY POTENTIOMETRIC AND CATALYTIC THERMOMETRIC TITRATION

Substance titrated	Taken, *g*	Potentiometric titration			Catalytic thermometric titration		
		No. of titrs.	Found, *g*	Average deviation, %	No. of titrs.	Found, *g*	Average deviation, %
Antipyrine	0·1000	3	0·1050	0·16	6	0·1046	0·53
Brucine	0·1000	3	0·1198	0·09	5	0·1214	0·43
Sodium acetate	0·0200	3	0·0199	0·25	5	0·0201	0·00

TABLE III.—COMPARISON OF RESULTS OBTAINED BY POTENTIOMETRIC AND CATALYTIC THERMOMETRIC TITRATION BY COULOMETRIC GENERATION OF TITRANT

Substance tritated	Potentiometric titration			Catalytic thermometric titration		
	No. of titrs.	Found, *mg*	Average deviation, *mg*	No. of titrs.	Found, *mg*	Average deviation, *mg*
Dimethylaniline	5	3·29	0·03	5	3·30	0·03
Pyridine	5	1·75	0·01	6	1·74	0·03
Triethylamine	5	2·44	0·03	7	2·42	0·03

Titrations in nitromethane

As solvent we used nitromethane, BDH Laboratory Reagent, containing 0·30% of water.[6] Other chemicals, solutions and apparatus used, as well as working conditions, were the same as in the titrations in acetic acid. Antipyrine (K_b in aqueous media 4×10^{-13}) was determined by potentiometric titration in different solvents, and the curves obtained are presented in Fig. 4. It can be seen that the potential change at the titration end-point in nitromethane is twice as great as that in acetic acid. Antipyrine cannot be determined by catalytic thermometric titration in acetic acid,[2] but we were able to perform this titration in nitromethane containing 2% of water and 8% of acetic anhydride. The results obtained agree with those of potentiometric titrations, the average deviation amounting to ±0·5%.

Titrations in acetic anhydride

The recording of temperature changes enabled us also to follow accurately the large temperature changes taking place when catalytic thermometric titrations are made in acetic anhydride. The solvent used in catalytic thermometric titrations consisted of acetic anhydride C. Erba, s.g. 1·08, min. 97% with 2% of water. We made potentiometric titrations of antipyrine in pure acetic acid, in a mixture of acetic acid with 8% of acetic anhydride, and in pure acetic anhydride, in which there is the highest potential jump at the titration end-point (Fig. 4). The results of catalytic thermometric titrations of antipyrine were the more precise the higher the concentration of acetic anhydride.

For the purpose of a thorough study of catalytic thermometric titrations in acetic anhydride, we first established the changes in the rate of hydrolysis of acetic anhydride as a function of the catalyst concentration, as we did for determination in acetic acid.[2] It is evident from the results Table II that in acetic anhydride even antipyrine can be successfully determined, and it is, therefore, to be expected that so could other weak bases which are impossible to determine in acetic acid.

Continuous addition of the titrant can be replaced by coulometric generation of hydrogen ions at the anode, according to Mather and Anson's method.[7] The solution titrated should contain, in addition to the base, acetic anhydride and acetic acid (in the ratio 7:1) 0·1*M* sodium perchlorate and 2% water. The optimal current density at the anode is 0·4 mA/cm^2, and the total volume of the anolyte 25 ml. Some of the results obtained by this coulometric technique are given in Table III.

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Summary—Catalytic thermometric titrations have been developed for bases (brucine, diethylaniline, potassium acetate and triethylamine) in acetic acid by continuous and discontinuous addition of the standard solution and automatic temperature recording. The determination of weak bases, *e.g.*, antipyrine, unsuccessful in acetic acid by catalytic thermometric titration, has been achieved by using nitromethane or acetic anhydride as solvent. Catalytic thermometric titrations were also performed by coulometric generation of hydrogen ions for the determination of micro amounts of weak bases in a mixture of acetic anhyride and acetic acid.

Zusammenfassung—Zur Bestimmung von Basen (Brucin, Diäthylanilin Kaliumacetat und Triäthylamin) in Essigsäure wurden katalytische thermometrische Titrationen mit kontinuierlicher und diskontinuierlicher Zugabe der Standardlösung und automatischer Temperaturregistrierung entwickelt. Die Bestimmung schwacher Basen, z.B. Antipyrin, die in Essigsäure durch katalytische thermometrische Titration nicht möglich ist, wurde durch Verwendung von Nitromethan oder Acetanhydrid als Lösungsmittel erreicht. Auch mit coulometrischer Erzeugung von Wasserstoffionen zur Bestimmung von Mikromengen schwacher Basen in einem Gemisch von Acetanhydrid und Essigsäure wurden katalytische thermometrische Titrationen ausgeführt.

Résumé—On a élaboré des titrages thermométriques catalytiques pour des bases (brucine, diéthylaniline, acétate de potassium et triéthylamine) en acide acétique par addition continue et discontinue de la solution étalon et enregistrement automatique de la température. Le dosage de bases faibles, par exemple l'antipyrine, qui n'a pu être effectué avec succès en acide acétique par titrage thermométrique catalytique, a été réalisé par l'emploi, comme solvant, du nitrométhane ou de l'anhydride acétique. Les titrages thermométriques catalytiques ont aussi été exécutés par génération coulométrique d'ions hydrogène pour le dosage de microquantités de bases faibles dans un mélange d'anhydride et d'acide acétiques.

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Estimation of dimethylsulphoxide with chloramine-T

(*Received* 21 *December* 1967. *Accepted* 9 *February* 1968)

DIMETHYLSULPHOXIDE is an unusually versatile chemical which has a very wide application as a solvent, a reaction medium and a chemical reactant,[1] and it is desirable to have a suitable procedure for its determination.

Earlier methods were based on either its reduction to dimethylsulphide by Sn(II),[3] Ti(III)[3,4] or iodide,[5] or its oxidation to dimethylsulphone by potassium permanganate.[6] Of the reductimetric methods, the most reliable involves oxidation of iodide in glacial acetic acid in presence of acetyl chloride[5] and titration of the iodine liberated, but does not work in dilute aqueous media. Potassium permanganate in acid medium is the only reagent so far recommended for the oxidimetric determination. Permanganate is reduced only to MnO_2 and not to Mn(II) by dimethylsulphoxide.

During the present study we examined the behaviour of dimethylsulphoxide (DMSO) towards dichromate, cerium(IV), vanadate, hypoiodite, hypochlorite and chloramine-T under various conditions. No oxidation of DMSO was observed with Cr(VI), Ce(IV) and V(V) in $1M$ sulphuric acid at room temperature. Even at ~80° with $2M$ sulphuric acid very little Ce(IV) or Cr(VI) reacted with $0{\cdot}1M$ dimethylsulphoxide. Addition of common catalysts such as osmic acid and molybdate was of no avail. Sodium hypochlorite oxidized DMSO to a limited extent in alkaline medium, and extensively in acid medium, but it was difficult to standardize the conditions. However, the reaction between chloramine-T and DMSO was found to proceed under suitable conditions in 1:1 stoichiometry according to the equation, $(CH_3)_2SO + \{CH_3 . C_6H_4SO_2NCl^-\} Na^+ + H_2O \rightarrow (CH_3)_2SO_2 + CH_3 . C_6H_4SO_2NH_2 + Na^+ + Cl^-$. Determination of DMSO by direct titration with chloramine-T was not practicable because the oxidation, though rapid, was not instantaneous, and a back-titration procedure was developed. The method is quicker than the permanganate method and just as accurate.

EXPERIMENTAL

An approximately $0{\cdot}025M$ aqueous solution of DMSO(Fluka) was prepared and standardized by the permanganate method.[6] Approximately $0{\cdot}05N$ aqueous chloramine-T solution was prepared and standardized iodometrically by the procedure of Bishop and Jennings.[7] All other reagents were of

Résumé—On a élaboré des titrages thermométriques catalytiques pour des bases (brucine, diéthylaniline, acétate de potassium et triéthylamine) en acide acétique par addition continue et discontinue de la solution étalon et enregistrement automatique de la température. Le dosage de bases faibles, par exemple l'antipyrine, qui n'a pu être effectué avec succès en acide acétique par titrage thermométrique catalytique, a été réalisé par l'emploi, comme solvant, du nitrométhane ou de l'anhydride acétique. Les titrages thermométriques catalytiques ont aussi été exécutés par génération coulométrique d'ions hydrogène pour le dosage de microquantités de bases faibles dans un mélange d'anhydride et d'acide acétiques.

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During the present study we examined the behaviour of dimethylsulphoxide (DMSO) towards dichromate, cerium(IV), vanadate, hypoiodite, hypochlorite and chloramine-T under various conditions. No oxidation of DMSO was observed with Cr(VI), Ce(IV) and V(V) in $1M$ sulphuric acid at room temperature. Even at ~80° with $2M$ sulphuric acid very little Ce(IV) or Cr(VI) reacted with $0{\cdot}1M$ dimethylsulphoxide. Addition of common catalysts such as osmic acid and molybdate was of no avail. Sodium hypochlorite oxidized DMSO to a limited extent in alkaline medium, and extensively in acid medium, but it was difficult to standardize the conditions. However, the reaction between chloramine-T and DMSO was found to proceed under suitable conditions in 1:1 stoichiometry according to the equation, $(CH_3)_2SO + \{CH_3 . C_6H_4SO_2NCl^-\} Na^+ + H_2O \rightarrow (CH_3)_2SO_2 + CH_3 . C_6H_4SO_2NH_2 + Na^+ + Cl^-$. Determination of DMSO by direct titration with chloramine-T was not practicable because the oxidation, though rapid, was not instantaneous, and a back-titration procedure was developed. The method is quicker than the permanganate method and just as accurate.

EXPERIMENTAL

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In the preliminary studies, known amounts of DMSO solution were taken and after adjustment of reaction conditions a known excessive volume of chloramine-T solution was added last, the volumes being so adjusted that the final volume was about 125 ml. After standing for various intervals of time at room temperature, the amount of chloramine-T left unconsumed was determined by addition of excess of potassium iodide followed by excess of sulphuric acid, and titration with thiosulphate of the iodine liberated. Dimethylsulphoxide and its oxidation products were found to have no action on potassium iodide in dilute solutions. The extent of oxidation was determined from ratio of the number of mmoles of chloramine-T consumed under the reaction conditions to the number of mmoles of DMSO taken.

RESULTS AND DISCUSSION

A representative set of results for the extent of oxidation of DMSO in 20 min by only a small excess of chloramine-T is given in Table I. It is seen that in the absence of chloride ions (other than the very low concentration resulting from progressive consumption of chloramine-T) the oxidation of dimethylsulphoxide is very slow at pH < 1. Oxidation occurred appreciably in the pH range 2·65–5·05 and again decreased at pH > 5·35. The rate of oxidation was greatest at pH 4–4·5. Thus, at pH 2·65 DMSO was quantitatively oxidized to dimethylsulphone in 10 min with a 20% excess of chloramine-T present, and in less than 5 min at pH 4–4·5 with the same excess of oxidant. When 75–100% excess of chloramine-T was used, oxidation was complete within a minute in the pH range 2·65–5·05.

TABLE I.—EXTENT OF OXIDATION OF DIMETHYLSULPHOXIDE WITH CHLORAMINE-T(CAT)

Medium	CAT consumed, *mmole*	$\frac{\text{mmole CAT used}}{\text{mmole DMSO taken}}$
0·5N H_2SO_4	0·2403	0·486
0·3N H_2SO_4	0·2939	0·594
0·1N H_2SO_4	0·3658	0·740
pH 2·65	0·4902	0·991
pH 3·15	0·4912	0·993
pH 3·45	0·4929	0·997
pH 3·75	0·4950	1·00
pH 4·00	0·4950	1·00
pH 4·45	0·4941	0·999
pH 4·75	0·4950	1·00
pH 5·05	0·4918	0·995
pH 5·35	0·4685	0·947
pH 7·7	0·0302	0·062
pH 8–9	0·0058	0·026

DMSO taken = 0·4946 mmole; CAT taken = 0·5588 mmole; temperature 25–30°C; standing time = 20 min.

At very low pH, chloride ion was found to affect the oxidation adversely, a larger amount of oxidant being used than expected from the normal stoichiometry. This clearly indicates that at low pH, chloride ion favours a side-reaction, presumably partial chlorination of the methyl groups, which entails extra consumption of oxidant. The side-reaction was observed to occur to a greater extent when

DMSO was added to chloramine-T solutions than *vice versa*. Studies on the mechanism of the oxidation are in progress. In the pH range 2·65–5, the presence of concentrations of chloride ion up to 0·1*M* did not affect the oxidation and the product was exclusively dimethylsulphone.

Recommended procedure

Adjust to 4–4·5 the pH of the aqueous solution containing 0·2–1 mmole of dimethylsulphoxide, using sodium acetate–acetic acid buffer. Dilute to 100–150 ml, add a known volume (~30% excess) of 0·1–0·2*N* chloramine-T solution, and after a minute, add 20 ml of 10% potassium iodide solution followed by excess of 2*M* sulphuric acid. Titrate the liberated iodine with thiosulphate. Run a blank with chloramine-T solution alone. The amount of DMSO (y) in the test solution is given by the equation

$$y = 39{\cdot}07N(V_1 - V_2)\text{g}$$

where N is the normality of the thiosulphate solution, V_1 is the volume of thiosulphate consumed in the blank and V_2 is the volume of thiosulphate used to titrate the excess of chloramine-T left over after the DMSO oxidation. The values obtained are accurate to within 0·5%.

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Summary—A rapid and accurate method for the estimation of dimethylsulphoxide has been developed based on its oxidation to dimethylsulphone at room temperature by chloramine-T at pH 4–4·5. The effect of variables such as the pH, the mode of addition of reagents and the concentration of chloride ion on the extent and nature of oxidation has been studied and optimal conditons for analytical determination of dimethylsulphoxide derived.

Zusammenfassung—Eine einfache und schnelle Methode zur Bestimmung von Dimethylsulfoxid wurde entwickelt, die auf der Oxidation zu Dimethylsulfon bei Zimmertemperatur mit Chloramin T bei pH 4–4,5 beruht. Der Einfluß von Umständen wie pH, Art der Zugabe der Reagentien und Chloridkonzentration auf Ausmaß und Natur der Oxidation wurde untersucht und die optimalen Bedingungen zur analytischen Bestimmung von Dimethylsulfoxid ermittelt.

Résumé—On a élaboré une méthode rapide et précise pour estimer le diméthylsulfoxyde, basée sur son oxydation en diméthylsulfone à température ordinaire par la chloramine T à pH 4–4,5. On a étudié l'influence de variables telles que le pH, le mode d'addition des réactifs et la concentration de l'ion chlorure sur le degré et la nature de l'oxydation, et l'on en a déduit les conditions optimales pour la détermination analytique du dyméthylsulfoxyde.

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Studies on metallochromic indicators—III

Hematoxylin and hematein

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HEMATOXYLIN has been reported to be an excellent indicator for the direct EDTA titration of aluminium,[1] thorium,[2] zirconium,[3] bismuth,[3] copper[4,5] and vanadium(IV).[6] It has also been found to form pink, violet or blue complexes with Ga^{3+}, In^{3+}, Fe^{3+}, Hg^{2+}, Pb^{2+}, Cd^{2+} Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+} and rare earths under suitable conditions. These chelates are less stable than the corresponding EDTA complexes, which, together with the sharpness of colour change, makes this dye a versatile complexometric indicator. Another good metallochromic indicator, unexplored as yet, is the oxidized form of hematoxylin, hematein, which behaves similarly. The present communication describes the conditions for its use in direct EDTA titrations, which can be classified according to the pH range used: (1) acetate buffers (pH 1–5·5) for Th^{4+}, Zr^{4+}, Bi^{3+}, Al^{3+}, VO^{2+}, In^{3+}, Ga^{3+}, Fe^{3+} and Hg^{2+}; (2) hexamine buffers (pH 5–7) for Pb^{2+}, Cd^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, Nd^{3+}, Pr^{3+}, Sm^{3+}, Gd^{3+} and Er^{3+}; (3) pyridine buffers (pH 6·5–8·5) for Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Zn^{2+}; (4) ammonia buffers (pH 8·5–9·5) for Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+} and Mg^{2+}. These dyes also make possible the successive titration of some pairs of metal ions.

One of the metals must be bismuth, and the other Al^{3+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+} or Er^{3+}.

Taylor[1] titrated EDTA (in hot solution in presence of acetate buffer) with aluminium, using hematoxylin as indicator. The titration was done this way round to avoid interference due to precipitation of basic aluminium acetate. However, if lactic or glycollic acid is present, basic aluminium acetate is not precipitated and the reverse titration is unnecessary. Furthermore, the direct titration under these conditions gives a sharper colour change at the end-point and is more accurate, and can be used for titrating Al in a mixture of cations.

EXPERIMENTAL

Reagents

Buffer solutions. Prepared by mixing in appropriate volumes (1) 0·1*M* sodium or ammonium acetate with 0·1*M* nitric or acetic acid; (2) 5% hexamine solution with 0·1*M* nitric acid; (3) 0·1*M* pyridine with 0·1*M* acetic acid; (4) 0·1*M* ammonium chloride with 0·1*M* ammonia solution. The final pH of the buffers was checked with a pH meter.

Indicator solutions. Ethanolic solutions (0·2%) of hematoxylin and hematein.

1,10-*Phenanthroline solution*, 0·05*M*. Dissolve 2·95 g of 1,10-phenanthroline in nitric acid and dilute to 250 ml with water.

Lactic and glycollic acids. Used as 90% aqueous solutions.

Procedure A—titration of single metal ions

Mix 10 ml of ~0·02*M* metal ion solution with an equal volume of the required buffer, add 5–6 drops of indicator, dilute to 100 ml, and titrate with 0·02*M* EDTA. The conditions of the titration and the colour change at the end-point are described in Table I. For titration of aluminium, add 0·5 ml of lactic or glycollic acid before pH adjustment.

Procedure B—bismuth and another ion

Adjust 10 ml of sample (total metal ion concentration ~0·02*M*) to pH 1–2 by adding 5 ml of acetate–nitric acid buffer, dilute to 100 ml and add 4–5 drops of indicator. Titrate the violet solution with 0·02*M* EDTA until a sharp colour change to yellow indicates the bismuth end-point. Raise the pH of the solution by adding dropwise (*i*) 20% ammonium acetate solution for Al^{3+} (add 0·5 ml of lactic or glycollic acid before raising the pH, and titrate in hot solution), (*ii*) pyridine for Cu^{2+}, (*iii*) 20% hexamine solution for other metal ions, until the colour of the indicator complex of the second metal ion is obtained. Titrate the second metal ion with EDTA.

*Procedure C—*Al, Bi, Cu *and* Pb *alloy*

Dissolve 2 g of alloy in nitric acid, evaporate the solution to small volume and dilute it to 1 litre. Take 50 ml of the sample solution and adjust the pH to 1–2 with 0·2*M* sodium acetate. Add 5–6

TABLE I.—EDTA TITRATIONS OF VARIOUS METAL IONS, WITH HEMATOXYLIN AND HEMATEIN AS INDICATORS

Metal ion	Temperature, °*C*	Buffer type	pH	Colour change	Optimum range *mg/100 ml*
Zr^{4+}	80–90	1*	1·0	Purple to yellow	20–50
Th^{4+}	room	1*	1·5	Pink to yellow	1–50
Bi^{3+}	room	1*	1·0	Violet to yellow	0·5–100
VO^{2+}	room	1*	4·0	Violet to greenish yellow	0·1–15
Ga^{3+}	room	1*	3·0	Purple to yellow	5–50
In^{3+}	room	1*	3·5	Pink to yellow	5–50
Al^{3+} (In presence of glycollic or lactic acid)	100°	1†	5·5	Violet to yellow	5–200
Pb^{2+}	room	2	5·5	Blue to yellow	1–100
Zn^{2+}	room	2	5·5	Blue to yellow	5–100
Cd^{2+}	room	2	5·5	Blue to yellow	20–100
‡Rare Earths	room	2	5·5–6·0	Blue or Blue-Violet to yellow	5–200
Cu^{2+}	room	3	6–6·5	Violet blue to yellowish green	0·5–30
Ni^{2+}, Co^{2+}	60–70	3	6·5–7·0	Violet to deep red	5–50
Mn^{2+}, Zn^{2+}	room	3	7–7·5	Violet to deep red	1–100
Ni^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}	room	4	9·0	Violet or blue-violet to deep red	5–100
Mg^{2+}	room	4	9·5	Violet to deep red.	5–100

* Sodium acetate.

† Ammonium acetate.

‡ La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Er^{3+}.

drops of indicator and titrate the violet solution with 0·001*M* EDTA to a yellow end-point (Bi content). Add a measured excessive volume of 0·05*M* EDTA and adjust the pH of the solution to 5–6*M* with hexamine. The solution turns yellow. Boil it for 5 min, cool, and titrate the excess of EDTA with 0·05*M* lead nitrate to a red-violet and end-point (sum of Al, Cu and Pb). Add 10 ml of 1,10-phenanthroline solution to displace EDTA from its copper complex, and titrate the liberated EDTA with lead nitrate solution (Cu content).

Take a second aliquot of the sample solution and titrate the bismuth with EDTA. Add a measured excessive volume of 0·05*M* EDTA and solid ammonium fluoride (1–1·2 g) to mask aluminium. Dilute to 150 ml, adjust the pH to 5–6 with hexamine, and titrate the excess of EDTA at 50–60° with 0·01*M* copper(II) (this gives Cu + Pb). The colour change at the end-point is from reddish yellow to violet. Calculate the lead and aluminium by difference.

Procedure D—*Aluminium bronze*

Apply the same procedure as that described by Přibil and co-workers,[7] but use hematoxylin or hematein instead of Xylenol Orange as indicator.

Procedure E—Ti *and* Al *alloy*

Dissolve 2 g of the alloy in 4*M* sulphuric acid. Filter off any insoluble material, ignite it, fuse it with potassium hydrogen sulphate in a platinum crucible, dissolve the cooled mass in water and mix this solution with the filtrate. Transfer the solution to a 1-litre volumetric flask and dilute to volume with water.

To 25 ml of the sample solution add a measured excessive volume of 0·05*M* EDTA and dilute with water to about 100 ml. Adjust the pH to 5·5–6 with hexamine, boil for 10 min, cool to 10–15°, add 0·5 ml of indicator and back-titrate the excess of EDTA, slowly and with constant shaking, with 0·05*M* bismuth nitrate to a pink end-point (sum of Ti and Al). Add 1·5 ml of lactic or glycollic acid (for up to 1·0 g of titanium) and adjust the pH to 5·5–6 with hexamine. The lactic acid displaces EDTA equivalent to the titanium and the solution becomes yellow. Cool the solution below 15° and titrate it with 0·05*M* bismuth nitrate to a pink-red end-point (Ti content).

Procedure F—Al *and* Ni *alloy*

Dissolve 1·0 g of alloy in hot nitric acid. Evaporate the solution to small volume, dilute with 200 ml of water and boil for 10 min. Cool, transfer the solution to a 1-litre volumetric flask and dilute to volume with water.

To 20 ml of sample solution add 2 ml of lactic acid (for up to 25 mg of aluminium) and 20 ml of 40% ammonium acetate solution. Dilute to 150 ml with water, adjust the pH to 5·5–6, boil, add 0·5 ml of indicator and titrate it hot with 0·05*M* EDTA to a bright yellow end-point (Ni + Al content). Use a magnetic stirrer to mix the solution during titration.

To a second 20 ml aliquot add a measured excessive volume of 0·05*M* EDTA, about 1 g of solid ammonium fluoride and 10 ml of 40% ammonium acetate solution. Dilute the solution to 150 ml, adjust the pH to 5·5–6 and add 0·5 ml of indicator. Titrate the excess of EDTA with 0·05*M* copper(II) to a red-violet end-point (Ni content).

RESULTS AND DISCUSSION

Hematoxylin is yellow below pH 6, red between pH 6 and 7 and red-purple above pH 7, while hematein is yellow below pH 6 and red above pH 7. Iron(III) and mercury(II) cannot be titrated owing to the gradual and indistinct change of colour at the end-point. Moreover, the reaction of mercury(II) with these indicators is very slow.

The colour change at the end-point is sharper in acidic media than in alkaline (Table I). In acidic media, these indicators are comparable to Xylenol Orange[3] for accuracy and sharpness of colour change. Even in dilute solutions (0·001*M*) the end-points are sharp and take place with addition of less than one drop of titrant. In alkaline media the complete colour change at the end-point requires about 0·08 ml of 0·001*M* EDTA. The average error was ±3–5 parts per 1000.

In titration of bismuth no interference is found from aluminium, rare earths and a number of bivalent metal ions. Moreover, these ions do not form complexes with hematoxylin or hematein at pH 1–2, so a successive determination of bismuth and one of these cations can be carried out by appropriate pH adjustments (*Procedure B*). Although thorium and zirconium can be titrated in presence of bivalent and tervalent metal ions without interference at pH 1–2, subsequent determination of another ion in the same solution is not possible, because thorium and zirconium block the indicator at pH 5–6 even in presence of EDTA, presumably on account of formation of ternary complexes (*cf.* Přibil[9]).

The results of the analysis of four aluminium alloys are given in Table II. The results are correct within experimental error. Chen and Li[10] used lactic acid for masking titanium, and this has been

TABLE II.—RESULTS OF THE ANALYSIS OF ALUMINIUM ALLOYS

Alloy composition, %				% found			
Bi,	0·45;	Cu,	6·6;	Bi,	0·44;	Cu,	6·5;
Pb,	0·55;	Al,	92·4;	Pb,	0·50;	Al,	92·6
Al,	8·8;	Cu,	85·9;	Al,	9·0;	Cu,	85·0;
Fe,	2·67;	Zn,	0·94;	Fe,	3·1		
Mn,	0·27;	Ni,	1·16				
Ti,	37·70;	Al,	57·43;	Ti,	37·8;	Al,	57·3
C,	4·87						
Al,	50·0;	Ni,	50·0	Al,	50·0;	Ni,	50·0

utilized to displace EDTA from the titanium complex. Přibil[11] introduced 1,10-phenanthroline for masking copper and other ions; this also has been utilized here in a displacement reaction.

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Summary—The use of hematoxylin and hematein as metallochromic indicators in direct EDTA titration of Zr^{4+}, Th^{4+}, Bi^{3+}, VO^{2+}, Ga^{3+}, In^{3+}, Al^{3+}, Pb^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+}, and a few rare earths is described. Aluminium is titrated directly in presence of acetate buffer, lactic or glycollic acid being used as auxiliary complexing agent. Mixtures of two metal ions can be titrated if one is Bi^{3+} and the other Al^{3+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+} or Er^{3+}. Aluminium alloys can be analysed *via* EDTA titrations, with these indicators.

Zusammenfassung—Der Gebrauch von Hämatoxylin und Hämatein als metallochrome Indikatoren bei der direkten EDTA-Titration von Zr^{4+}, Th^{4+}, Bi^{3+}, VO^{2+}, Ga^{3+}, In^{3+}, Al^{3+}, Pb^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+} und einigen seltenen Erden wird beschrieben. Aluminium wird direkt in Gegenwart von Acetatpuffer titriert, wobei Milch- oder Glykolsäure als Hilfskomplexbildner dienen. Mischungen von zwei Metallionen können titriert werden, wenn das eine Bi^{3+} und das andere Al^{3+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+} oder Er^{3+} ist. Aluminiumlegierungen können mit diesen Indikatoren über EDTA-Titrationen analysiert werden.

Résumé—On décrit l'emploi de l'hématoxyline et de l'hématéine comme indicateurs métallochromes dans les titrages directs à l'EDTA de Zr^{4+}, Th^{4+}, Bi^{3+}, VO^{2+}, Ga^{3+}, In^{3+}, Al^{3+}, Pb^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+} et de quelques terres rares. On titre l'Aluminium directement en présence de tampon acétate, les acides lactique ou glycolique étant utilisés comme agents complexants auxiliaires. On peut titrer des mélanges de deux ions métalliques si l'un deux est Bi^{3+} et l'autre Al^{3+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+} ou Er^{3+}. On peut analyser les alliages d'aluminium par titrages EDTA avec ces indicateurs.

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Iron(III) complexation with 2,3-pyridinediol

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Ortho-DIHYDROXY compounds are known to form complexes with iron.[1-5] In the present note, the complexation of iron(III) with a biochemically important compound, 2,3-pyridinediol, is examined. The compound is recommended as a sensitive and selective reagent for spectrophotometric determination of iron.

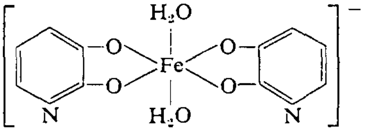
EXPERIMENTAL

Reagents

2,3-Pyridinediol was obtained from Aldrich Chemicals, and used as its light brown solution in ethanol. Iron(III) perchlorate was used in solution acidified with perchloric acid.

Spectral investigations

2,3-Pyridinediol has maximum absorption at 240 and 298 mμ, the corresponding molar absorptivities being $4\cdot4 \times 10^{-3}$ and $7\cdot5 \times 10^{3}$. A mixture of iron(III) and ligand ($\sim 10^{-4}M$) has a colour varying from sky-blue to purple-red according to the acidity. The absorption maximum lies at about 550 mμ, shifting towards lower wavelengths with decrease in acid concentration until it lies at 500 mμ at pH 3·5; it remains at this wavelength up to pH 8·0. The intensity of the colour increases from pH 0 to pH 2 but remains unaltered in the pH range 4·5–7·5. In this pH range (4·5–7·5) a tenfold molar excess of reagent is sufficient for full development of the colour. The system obeys Beer's law up to 5·0 ppm of iron and its sensitivity is 0·011 μg/cm² for 0·001 absorbance. The composition of the complex at pH > 5·0 was deduced by the mole-ratio method and found to be 1:2 (Fe:ligand). Structure I is proposed for the complex, the 6-co-ordination of iron being supposed to be completed by water molecules. The method of continuous variations indicated that a 1:1 complex exists at higher acidity, so to avoid complications arising from the stepwise equilibria, it is best to determine iron with 2,3-pyridinediol at pH 4·5–7·5.



I

The amounts of foreign ions (in ppm) tolerated in estimation of 2·0 ppm of iron at pH 5·0 are: Tl(I) 200, Ni 200, Co(II) 200, Cd 200, Pb 200, Hg(II) 200, Zn 200, Mg 200, Sr, 200, Ba 200, Be 150, Sn(II) 60, Sb(III) 40, Th 200, Ti(IV) 100, Zr 100, F^- 200, Cl^- 400, Br^- 400, I^- 400, CH_3COO^- 400, IO_3^- 200, $S_2O_3^{2-}$ 200, PO_4^{3-} 400, borate 400 and tartrate 400. Titanium and zirconium can be masked with sodium fluoride; Ag, Cu(II), Mn(II), Al, Cr(II), Ce(IV), V(V), U(VI), oxalate and citrate interfere.

In 0·6*M* perchloric acid medium the 1:1 complex obeys Beer's law from 0·5–12·0 ppm of iron at 550 mμ, the sensitivity being 0·039 μg/cm² for 0·001 absorbance. For 5·0 ppm of iron an 80-fold molar excess of reagent is needed. A study of interferences showed that at this acidity 500 ppm each of Ag, Tl(I), Cu(II), Ni, Co(II), Cd, Pb, Hg(II), Zn, Mg, Sr, Mn(II), Ba, Be, Al, Th, U(VI) and 1000 ppm of citrate, tartrate, borate, Br^- and Cl^- could be tolerated, but Sn(II), Cr(III), Ti(IV), Zr, Ce(IV), V(V), IO_3^-, I^-, $S_2O_3^{2-}$ and $C_2O_4^{2-}$ cause serious interference.

Attempts to obtain a mixed ligand complex by adding pyridine to a mixture of iron(III) and 2,3-pyridinediol solutions and standing the solution over conc. sulphuric acid in a vacuum desiccator yielded a deep purple solid which on analysis gave C 38·6%, H 3·4%, N 9·1%, in agreement with structure I (requires C 38·6%, H 3·5%, N 9·0%).

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Summary—Iron(III) complexation with 2,3-pyridinediol has been investigated with a view to ascertaining the structures of the complexes formed and examining the analytical potential of this biochemically important ligand.

Zusammenfassung—Die komplexe Bindung von Eisen (III) mit 2,3-Pyridindiol wurde untersucht im Hinblick auf die Strukturen der gebildeten Komplexe und auf die analytischen Möglichkeiten dieses biochemisch wichtigen Liganden.

Résumé—On a étudié la complexation du fer(III) avec le 2,3-pyridinediol afin de déterminer les structures des complexes formés et d'examiner les possibilités analytiques de ce ligand biochimiquement important.

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Separation of carrier-free silver from neutron-irradiated palladium

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Irradiation of palladium in a flux of thermal neutrons results in the "direct" formation of the radioactive isotopes listed in Table I. (The calculated values for the induced activity are rather approximate because of uncertainties in nuclear reaction cross-sections.) Palladium-111 and 111m decay to 7·5 d silver-111 through the 1·2 min silver-111m. The irradiation of palladium therefore provides a source of carrier free-silver-111. (About 2 mc will accumulate under the conditions of irradiation given in Table I.) A day or so after the irradiation only 13·6 hr and 17 d palladium and silver-111 are expected to be present.

TABLE I.—SOME RELEVANT PROPERTIES ASSOCIATED WITH ISOTOPES PRODUCED BY (n, γ) REACTIONS ON PALLADIUM

Isotope	Half-life	Mode of decay	Activity,* mc
^{103}Pd	17 d	EC	2
^{109}Pd	13·6 hr	β^-	400
^{109m}Pd	4·7 min	γ, β^-	10
^{111}Pd	22 min	β^-	4
^{111m}Pd	5·5 hr	γ, β^-	<1

* The approximate activity induced in 1 g of palladium irradiated in a neutron flux of 10^{12}n.cm^{-2}.sec^{-1} for 1 week.

Two methods are known to us for the separation of carrier-free silver from macro amounts of palladium. The method described by Hamilton *et al.*[1] for cyclotron-irradiated targets in which a number of radioisotopes of neighbouring elements are produced, is more elaborate and lengthy than is necessary for the present purpose. The second method, due to Schweitzer and Nehls,[2] is simple and rapid to perform but in our hands it gave poor recovery of silver which was not satisfactorily freed from palladium radioactivity. Part of the difficulty may arise in adjusting the solution to give good yields of silver in a radiocolloid form. A new method which is simple and rapid to perform and gives efficient separation of silver in high yield is described here. The well-known low stability of complexes formed by silver relative to that of those formed by palladium with complexan-type

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EXPERIMENTAL

Dowex chelating ion-exchange resin A1 (50–100 mesh) was obtained in the sodium form from the J. T. Baker Chemical Co., Phillipsburg, N.J., U.S.A. Before use it was converted into the hydrogen form by first stirring in a beaker with several portions of $2M$ nitric acid and then completing the exchange by preparing a column of the resin and washing it with the same acid. Finally the column was conditioned with $0{\cdot}5M$ nitric acid.

Finely divided palladium metal (*e.g.*, sponge) of high purity was irradiated in a thermal neutron flux of $1{\cdot}7 \times 10^{11}$ n.cm^{-2}. sec^{-1} for one week at the Atomic Energy Research Centre, Harwell, England. It was then dissolved in hot concentrated nitric acid and the solution evaporated to near dryness. The concentrate was diluted with water to give an acidity in the range $0{\cdot}1$–$0{\cdot}5M$.

The solution prepared from the irradiated palladium was placed on a resin column and the silver was eluted with $0{\cdot}1$–$0{\cdot}5M$ nitric acid. A resin column 12 cm long and 0·75 cm internal diameter is adequate for the retention of at least 5 mg of palladium. Over 95% of the silver is eluted in one column volume (5·3 ml in the example quoted). Elution is complete in 2–3 column volumes.

The silver-111 and palladium-109 were counted with the same counting efficiencies in solution in an annular type M6H Geiger-Müller counter (Twentieth Century Electronics Ltd., Croydon, England). In order to check the half-life of the silver, a sample was converted into silver iodide and counted over a period of 10 weeks with an end-window gas-flow proportional counter operating on a 90% argon/10% methane gas mixture. X-rays resulting from the electron capture process in the decay of palladium-103 were used in the detection and measurement of this isotope.

RESULTS AND DISCUSSION

It was concluded from batch experiments that palladium (labelled with palladium-103) in $0{\cdot}1$–$0{\cdot}5M$ nitric acid is taken up equally well, to a first approximation, by the chelating resin in the sodium, ammonium or hydrogen form. The use of the resin in either of the first two forms, however, results in the presence of sodium or ammonium ions in the effluent, and these are probably less desirable than hydrogen ions. The solution containing the silver eluted from a resin column in the hydrogen form did not give a visible solid residue on evaporation to dryness.

The radiochemical purity of the silver-111 was checked by adding carrier silver and palladium(II) nitrates to a sample and separating the palladium in a chemically pure form by precipitation with dimethylglyoxime from dilute nitric acid media. A decontamination factor (defined as the ratio of palladium present in the silver before and after separation) of $\geqslant 2 \times 10^5$ was estimated to result from the ion-exchange separation. (Induced activity data given in Table I for palladium-109 and the text for silver-111, along with counting rates measured with the Geiger-Müller counter, were used indirectly in this calculation.) The half-life of a sample of the silver separated on the resin two days after the irradiation was found to be in good agreement with published values. There was no evidence of contamination in this sample either by palladium-109 or 103 and the silver-111 could account for all of the initial activity of 5×10^4 cpm, thus providing additional evidence for a high degree of decontamination from palladium.

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Summary—The use of a chelate-forming ion-exchange resin for the separation of carrier-free silver-111 from neutron irradiated palladium is described.

Zusammenfassung—Die Verwendung eines chelatbildenen Ionenaustauschharzes zur Abtrennung von trägerfreiem Silber-111 aus neutronenbestrahltem Palladium wird beschrieben.

Résumé—On decrit l'emploi d'une résine échangeuse d'ions formant des chélates pour la séparation de l'argent-111 exempt d'entraîneur du palladium irradié aux neutrons.

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Correction of luminescence emission spectra by digital computer

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IT has been recommended that all published luminescence emission spectra be corrected for the spectral response of the detection system.[1-3] This is seldom necessary in routine analysis, but is vital to evaluate electronic energy levels or to make valid comparisons with data from other laboratories.

The correction process normally adopted involves reading off observed emission intensities from a recorded curve at a series of wavelengths and dividing each by the appropriate, predetermined, correction factor. Results are then generally normalized with respect to the maximum value; a process involving a further series of divisions. These calculations can be very time-consuming and, since the problem lends itself particularly well to digital processing, it is surprising that only one suitable program has so far been published.[3] Although excellent in most respects, this program is rather involved and difficult for the chemist of limited computer experience to assimilate. We feel that the following program fulfils the need for a simple procedure which could readily be adapted for individual requirements.

EXPERIMENTAL

Materials and methods

The construction of the luminescence spectrophotometer used in this work has been described previously.[4] The detection system was calibrated with a standard tungsten lamp by the method of Parker and Rees.[2] Since this laboratory is primarily concerned with the photochemical and luminescence properties of flavine systems the wavelength range covered was 490–700 mμ. Flavine mononucleotide (FMN), supplied by British Drug Houses Ltd., was chosen for the purpose of illustration and used without further purification.

Calculations were performed by an Elliott 803 Computer which employs a local form of Algol. The basic program reads as follows.

```
ALP 267
CORRECTION OF LUMINESCENCE EMISSION SPECTRA′
BEGIN REAL ARRAY S,A,B,X(1:43)′
    REAL L′ INTEGER I′
    L:=φ′
    FOR I:=1 STEP 1 UNTIL 43 DO
    READ S(I)′
    WAIT′
    FOR I:=1 STEP 1 UNTIL 43 DO
    BEGIN SWITCH SS:=M′
      READ A(I)′
      B(I):=A(I)/S(I)′
      IF B(I) LESS L THEN GOTO M′
      L:=B(I)′
    M: END′
      FOR I:=1 STEP 1 UNTIL 43 DO
      BEGIN X(I):=B(I)/L*100′
        PRINT 5*I + 485, SAMELINE, ££S2??, ALIGNED(3,1),X(I)
      END
END′
```

The expression ££S2?? provides a convenient format for the tabulated results and means "leave 2 spaces."

RESULTS

Curve *A* of Fig. 1 represents a typical recording of the fluorescence emission spectrum of FMN. The correction factors (in wave number-based units) are plotted, at 5-mμ intervals, as curve *S*. Dividing the ordinates of curve *A* by those of curve *S* results in a corrected emission spectrum (B, not illustrated). Normalization gives the final result shown in Fig. 2 (Curve X).

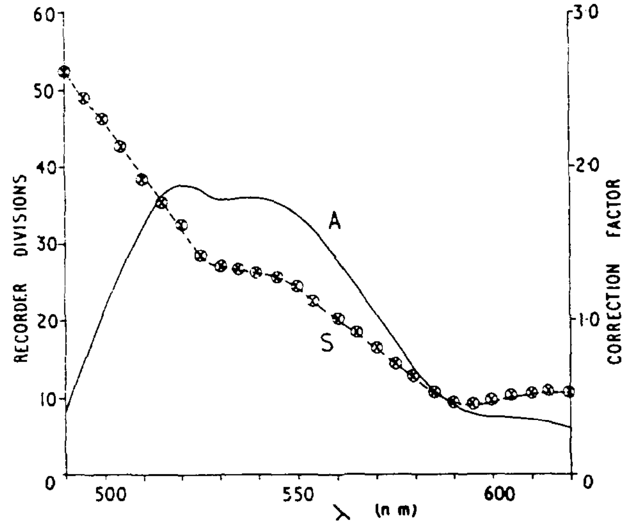

FIG. 1.—Curve *A*: Uncorrected fluorescence emission spectrum of 2·0 × $10^{-5}M$ FMN in 0·05*M* phosphate buffer at pH 7·0
Curve *S*: Correction data for the instrument, obtained with the aid of a standard tungsten lamp.

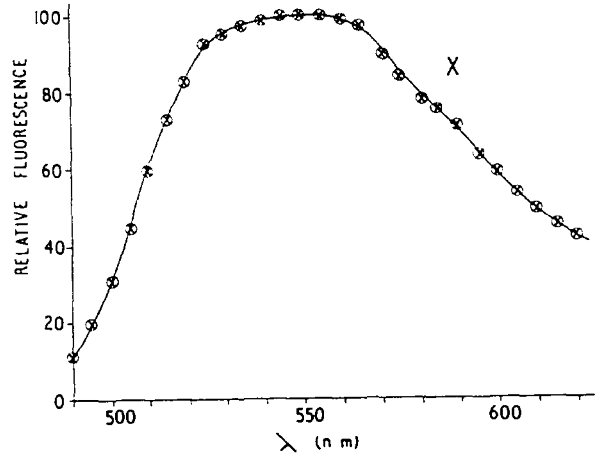

FIG. 2.—Corrected and normalized fluorescence emission spectrum of FMN.

Thus, in this case, a difference of 30 mμ in the wavelength for maximum fluorescence was apparent between observed and corrected spectra. In addition the hint of a secondary maximum ($\lambda_{\text{obs.}}$ = 540 mμ) and a shoulder ($\lambda_{\text{obs.}}$ = 605 mμ) disappeared upon correction. The apparent increase in sensitivity at 525 and above 600 mμ is due to grating anomalies in the monochrometer.

The advantage of using the digital computer for calculation, apart from accuracy, is in the time taken to perform the calculation [by slide rule (15·5 min), desk calculating machine (20 min) and computer (3 min)].

DISCUSSION

The program described treats data as arrays of 43 real numbers; there being 43 intervals of 5 mμ in the chosen wavelength range. In this type of treatment a fixed number of data must be supplied to the computer, 43 in this example. Should the entire range not be required it suffices to insert zero at each superfluous point on the data tape.

Since the correction factors, once determined, are semi-permanent in nature, it is convenient to attach them to the end of the program tape. At the point "WAIT" the experimental data may be fed in.

A linear wavelength scale was chosen for simplicity since the grating monochromator employed has linear dispersion with respect to wavelength. The integer counter (I) takes values from 1 to 43 which are converted into wavelengths in the print statement: 5*I + 485. For a different wavelength range and increment it is a simple matter to amend this statement and the size of the arrays. Should a linear energy spectrum be required the print statement could again be modified. For example "PRINT 1/(0·005*I + 0·485)" will give results in reciprocal microns.

The present print format produces two columns of figures representing wavelength and normalized corrected data. It should be a relatively simple matter to employ a digital plotter to give results directly in graphical form or to expand the program to allow integration of emission curves for determination of quantum yields.

Acknowledgement—We are indebted to Professor J. H. Turnbull for his interest and to Mr. A. Bowd for technical assistance.

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Summary—A simple Algol program for the correction of luminescence emisson spectra for instrumental variations is described. Suggestions are made as to how the program many be modified to suit individual requirements.

Zusammenfassung—Ein einfaches ALGOL-Programm zur Korrektur von Lumineszenzemissionsspektren für apparztive Einflüsse wird angegeben. Es werden Vorschläge gemacht, wie man das Programm zweckmäbig modifiziert, um individuellen Anforderungen zu genügen.

Résumé—On décrit un programme Algol simple pour corriger les spectres d'émission de luminescence des variations instrumentales. On apporte des suggestions sur la manière dont le programme peut être modifié pour convenir à des exigences particulières.

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LETTER TO THE EDITOR

Interference of the ammonium ion in Mohr's method for the determination of chloride

SIR,

With reference to the article "Interference of the ammonium ion in Mohr's method for the determination of chloride" in *Talanta*,[1] I should like to point out the following.

Since the end of the 1950's the theoretical approach to analytical problems has been simplified to a large degree by the introduction of conditional constants. Using these, it is possible, as Ringbom[2,3] has pointed out, to make a critical evaluation of different methods of analysis, *e.g.*, complexometric titration, acid–base and precipitation titration, ion-exchange, extraction, *etc.* It is often found that the correlation between the results obtained by experiment and those worked out theoretically is surprisingly high.

Unfortunately, in the article mentioned, dealing with chloride titration according to Mohr, the results have not been based on mathematical calculation even though all the stability constants necessary for a theoretical solution of the problem are available. At an ionic strength of 0·1 the following constants are valid.

Dissociation constants: $pk_{NH_4} = 9{\cdot}37$; $pk_{HCrO_4} = 6{\cdot}2$; $[Cr_2O_7^{2-}]/[HCrO_4^-]^2 = 10^{1\cdot5}$.

Stability constants: $\beta_{Ag(NH_3)} = 10^{3\cdot4}$; $\beta_{Ag(NH_3)_2} = 10^{7\cdot4}$.

Solubility products: $pS_{AgCl} = 9{\cdot}5$; $pS_{Ag_2CrO_4} = 11{\cdot}3$.

When chloride is titrated with silver ions the relative error is

$$E_{rel} = ([Ag^+]_{end} - [Cl^-]_{end})/C_{Cl}$$

where C_{Cl} equals the total concentration of chloride in the solution and $[Ag^+]_{end}$ and $[Cl^-]_{end}$ are the concentrations of silver and chloride ions at the end-point of the titration. If chromate with a total concentration of C_{CrO_4} is chosen as the indicator, and the pH value of the solution is approximately 7·2, then the formation of $HCrO_4^-$ ions may be ignored and the concentration of silver ions at the end-point will be

$$[Ag^+]_{end} = \sqrt{S_{Ag_2CrO_4}/C_{CrO_4}}.$$

The solubility product of silver chloride then decides the value of $[Cl^-]_{end}$ and it is found that

$$[Cl^-]_{end} = S_{AgCl}/[Ag^+]_{end} = S_{AgCl}\sqrt{C_{CrO_4}/S_{Ag_2CrO_4}}.$$

The formulae given above can be used to work out the error when titrating chlorides, if all interfering side-reactions, *e.g.*, the influence of ammonium ions, can be ignored. However, in those cases where the solution contains ammonium ions and the pH value of the solution is so low that the formation of $HCrO_4^-$ ions cannot be avoided, then the reactions affecting the final result should be taken into account by use of a conditional solubility product. Side-reactions may be taken into account by introducing suitable coefficients, the α-coefficients.[2,3]

The following conditional solubility products may be used:

$$S'_{AgCl} = \alpha_{Ag(NH_3)} S_{AgCl}$$

$$S'_{Ag_2CrO_4} = \alpha^2_{Ag(NH_3)} S_{Ag_2CrO_4}$$

where

$$\alpha_{Ag(NH_3)} = 1 + [NH_3]\beta_{Ag(NH_3)} + [NH_3]^2\beta_{Ag(NH_3)_2}.$$

The constants $\beta_{Ag(NH_3)}$ and $\beta_{Ag(NH_3)_2}$ are the overall stability constants for the two silver ammine complexes. It should be noted that in calculating $\alpha_{Ag(NH_3)}$, the fact that the ammonium ion dissociates should also be borne in mind, *i.e.*,

$$[NH_3] = C_{NH_3}/\alpha_{NH_3(H)}$$

where C_{NH_3} equals the total concentration of ammonium ion in the solution and $\alpha_{NH_3(H)} = 1 + [H_3O^+]10^{9\cdot37}$.

The general expression for the error in the analysis will then be

$$E_{rel} = \frac{\alpha_{Ag(NH_3)}\sqrt{S_{Ag_2CrO_4}/[CrO_4^{2-}]} - S_{AgCl}\sqrt{[CrO_4^{2-}]/S_{Ag_2CrO_4}}}{C_{Cl}}$$

In their work,[1] Block and Waters used an indicator consisting of a mixture of chromate and dichromate and in each titration added 20 drops of a solution containing 4·2 g of potassium chromate and 0·7 g of potassium dichromate per 100 ml of water. Taking into account the fact that the total volume used in each titration is 60 ml and that the pH value of the solution is approx. 6·7, the concentration of chromate ions in the solution, *i.e.*, the concentration which decides the value of $[Ag^+]_{end}$, can be calculated. The concentration of dichromate ions may be ignored in this case and it is found that $[CrO_4^{2-}] \sim 10^{-2\cdot5}$. The total amount of chloride in the solution is 30·4 mg, which corresponds to $C_{Cl} = 10^{-1\cdot85}$. When these values are introduced into the expression above, the relative error is found to be

$$E_{rel} = \alpha_{Ag(NH_3)}10^{-2\cdot55} - 10^{-3\cdot25}$$

In Table I, the error has been calculated for the amounts of ammonium nitrate referred to in the article. The errors are always positive.

TABLE I.—ESTIMATION OF ERROR IN TITRATION WHEN $[CrO_4^{2-}] = 10^{-2\cdot5}$ AND $C_{Cl} = 10^{-1\cdot85}$

NH_4NO_3 added, *g*	pC_{NH_3}	pH	$\log \alpha_{Ag(NH_3)}$	Error, % calc.	Error, % expt.
0·1	1·62	6·75	0·05	0·3	0
0·3	1·15	6·79	0·47	0·8	0·3
0·6	0·84	6·72	0·65	1·3	1·0
1·0	0·62	6·61	0·80	1·8	1·7
1·5	0·45	6·61	1·08	3·4	3·0
2·0	0·32	6·60	1·29	5·5	3·3

From this table it is clear that the error obtained by experiment agrees as well as can be expected with that obtained by theoretical calculation. When the concentration of ammonium ions rises the ionic strength of the solution is influenced and this in turn affects the values of the constants given above. Corrections for the constants depending on the ionic strength of the solution have not yet been worked out but they would only influence the results to a very slight degree.

It is, then, easy to calculate the error in analysis under different experimental conditions and, by varying the acidity of the solution and the amount of chromate, to arrive at the best conditions.

The conditions suggested by the authors of the article do not represent the optimum. In Table II the theoretical error when 2 g of ammonium nitrate are used in the analysis (*viz.*, last line of Table I) has been calculated for various values of the acidity of the solution and the amount of chromate added. Also included in the table is the degree of error obtained by experiment under these conditions.

TABLE II.—THEORETICAL AND EXPERIMENTAL ERROR OBTAINED WHEN TITRATING CHLORIDE WITH SILVER NITRATE IN THE PRESENCE OF 2 g OF NH_4NO_3

Total concentration of chromate, *M*	Error, % pH 6·6 calc.	Error, % pH 6·6 expt.	Error, % pH 6·4 calc.	Error, % pH 6·4 expt.	Error, % pH 6·2 calc.	Error, % pH 6·2 expt.
$10^{-2\cdot4}$	6·1	6·9	2·9	4·4	1·5	1·9
$10^{-2\cdot2}$	4·7	4·6	2·5	3·6	1·3	1·5
$10^{-2\cdot0}$	3·7	3·8	1·9	2·2	1·0	1·3

Volume of solution 60 ml; $C_{Cl} = 10^{-1\cdot85}$; experimental errors are means of three titrations.

An increase of the acidity of the solution and in the amount of chromate has a favourable influence on the result. No effect of the increased concentration of chromate on the colour of the precipitate was observed.

From what has been said it is shown that on the basis of theoretical calculation it is possible to obtain the best conditions for an experiment, *i.e.*, to improve the accuracy of analysis. Such an approach should always be carried out, if possible, when dealing with analytical problems. One condition for this, however, is that the stability constants for the different reactions in question are known.

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TALANTA REVIEW*

TERNARY COMPLEXES IN ANALYTICAL CHEMISTRY

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Summary—Reactions between a complex AB and a third component C do not always proceed by a displacement mechanism governed by the energy difference of the chemical bonds A—B and A—C. The third component often becomes part of the complex, forming a mixed co-ordination sphere or ternary complex. The properties of this ternary complex ABC are not additive functions of the properties of AB and AC. Such reactions are important in many methods in analytical chemistry, particularly in photometric analysis, extractive separation, masking, *etc.* The general properties of the four basic types of ternary complex are reviewed and examples given. The four types comprise the systems (*a*) metal ion, electronegative ligand, organic base, (*b*) one metal ion, two different electronegative ligands, (*c*) ternary heteropoly acids, and (*d*) two different metal ions, one ligand.

ONLY over the last 20–30 years have complex compounds begun to be widely used in analytical chemistry. To use a chemical reaction in analysis it is essential to know at least the equation for the interaction, and the binding energy between the components. Therefore the extent of knowledge about these two factors may define the scientific level of any section of analytical chemistry.

In the reference tables in the first edition (1938) of the well-known book by Latimer,[1] there were about 400 redox potentials, 200 solubility products and 150 dissociation constants for acids and bases, but only about 40 equilibrium constants for complexes, and most of these were concerned with metals such as silver and mercury and ligands such as halides and ammonia. In the preface to the first edition of his book on photometric analysis, Sandell[2] wrote that he felt very disturbed when he compared the wide application of colorimetric methods with the state of knowledge about those reactions on which the methods were based.

Over the past 20–30 years our knowledge of the chemistry of complex formation in solutions has developed tremendously. One of the main reasons for this was the development of new aspects of chemical technology, which demanded new methods of separating complex mixtures of elements, and methods for analysing semiconductor, radioactive, high-temperature resistant, and other materials. It was soon established that separation methods, important in technology and science, *e.g.*, solvent extraction and ion-exchange, were closely connected with complex formation equilibria. The use of organic reagents for precipitation, masking and titration was also a practical application of the chemistry of complex compounds. Photometric methods

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* For copies of this review see Publisher's advertisement near the end of this issue.

of analysis are almost all based on the chemistry of coloured complexes. Complex formation is also very important in polarography, amperometric titration, coulometry, *etc.* It is obvious that complex compounds are also important in biochemistry, particularly in the chemistry of enzymes, in homogeneous catalysis, and in many other fields.

All these factors have led to an intense development of equilibrium studies on solutions of complexes. Today, the composition of successively formed complexes and values of the stepwise stability constants have been established for the majority of metals and for many important ligands. Some time ago it might have been thought that solution of this part of the problem was nearing completion. It was assumed that it was possible to study each two-component metal–ligand system; if the composition and the constants were known, then the most favourable conditions for formation could be calculated. It was also assumed that it was easy to calculate the interaction between a given complex and a third component which could bind either the ligand or the central ion of the complex. For example, it was accepted that it was possible to calculate the equilibrium between the coloured titanium(IV) peroxide complex and oxalate ions, from the stability constants for the systems TiO^{2+}—H_2O_2 and TiO^{2+}—$C_2O_4{}^{2-}$, and the dissociation constants for hydrogen peroxide and oxalic acid. By analogy with other types of reactions between three components, *e.g.*, precipitation, it was accepted that the interaction was a competitive displacement of peroxide by oxalate to yield titanyl oxalate and hydrogen peroxide.

Mathematical difficulties which sometimes arise in such calculations, in particular because of the overlap of the stepwise equilibria, are merely technical and can be overcome by using computers or calculating machines, and sometimes some simplifications of the equations.

It turned out, however, that the reaction mechanism often does not conform to that of a simple metathesis and the reaction products have new properties which were quite impossible to foresee. Many researchers' work shows that the interaction of these components, two of which can replace each other, is more complicated than the simple reaction (1), resulting in a ternary complex, which may be of several types. That is, we do not always have a competitive displacement

$$AB + C \rightleftharpoons AC + B, \tag{1}$$

but

$$AB + C \rightleftharpoons ABC \tag{2}$$

The properties of the ternary compound differ from those of each of the possible binary compounds AB and AC, which can often exist separately. For a reaction of type (1) the system has additive properties at any position of the equilibrium and its absorption spectrum, redox potential and other properties can be calculated from the data for the binary compounds AB and AC; the relative amounts of the two complexes may be calculated from their stability constants and the total ("analytical") concentrations of B and C. For equilibria of type (2), on the other hand, the system is non-additive since the ternary compound ABC has properties which are not the sum of the properties of the equivalent concentrations of AB and AC. For this reason, the name mixed complexes is less correct than the name triple complexes, because the properties of a mixture would be additive.

If the reaction went according to scheme (1) it would be expected that when oxalate was introduced the spectral absorption band of the titanium(IV)–peroxide complex would gradually weaken but remain at the same wavelength of maximum absorption constant; the absorbance is indeed reduced, but the absorption peak shifts to shorter wavelengths. Similarly, the interaction of the blue copper(II)–pyridine complex with salicylate anions (Sal^{2-}), might be expected to lead to the green copper salicylate according to the reaction

$$[Cu^{2+} . py_2] + Sal^{2-} = CuSal + 2py. \tag{3}$$

However, in a mixture containing copper(II), pyridine and salicylate, a blue complex forms which has an absorption spectrum different from that of either binary compound and has a significantly higher molar absorptivity than either. What is more, the compound forming in the three-component system has many other properties which differ from those of either of the binary complexes. Thus the pyridine–copper and copper–salicylate complexes are not extracted by chloroform, but the product of the three-component system is easily extracted by chloroform. The composition of this compound, depending on the conditions, fits the formulae $[Cu . py_2]Sal$ or $[CuSal_2^{2-}] . 2[py . H^+]$.

There are examples of still more complicated relationships between binary and ternary systems. For example, iron(III) forms a yellow complex with EDTA over a wide range of pH, but does not generally form stable complex compounds with hydrogen peroxide in aqueous solutions, yet in a mixture of iron(III), hydrogen peroxide and EDTA, as is well-known, a violet complex forms at pH 10.[4]

At first such cases seemed the exception, but with the passing of time it became clear that there were many of these occurrences, and in some systems they were not the exception but the rule. The ternary complex may contain one metal and two different ligands, or one ligand and two different metals and can be said to have a mixed co-ordination sphere. It should be noted in passing that compounds such as $KFe(SCN)_4$ or $K_3Fe(CN)_6$ cannot possibly be considered as ternary complexes, as is sometimes thought, since in an aqueous solution potassium ions do not enter the complex groups, but are dissociated to leave the binary complex anions $Fe(SCN)_4^-$ and $Fe(CN)_6^{3-}$ respectively; X-ray analysis of the structure of the solids confirms that the potassium ions are not involved in complex formation.

The existence of complexes with a mixed co-ordination zone has long been known for many platinum, cobalt(III) and some other metal ions. However, the interaction in complexes of platinum or cobalt(III) is governed, in the main, by kinetic factors, and not by the thermodynamic stability. It is sufficient here to recall that for complexes of these metals *cis*- and *trans*-isomers often form, although the first are usually thermodynamically unstable and this is contrary to the usual pattern for equilibrium reactions of metal ions. It is accounted for by the kinetic slowness of reaction of these complexes, this inertness being conferred by the electronic configuration of the metal ions and by the reaction mechanisms concerned. With labile complexes the kinetics of the dynamic equilibrium are no longer a factor and the formation and reactivity of a complex are determined by the thermodynamic stability of the complex, *i.e.*, by the free energy change in the reaction.

This explains why in many cases there is a reaction of type (1) during the interaction of the three reacting components. Some researchers[5] draw attention to the fact that reactions of type (1) can also lead to the formation of complexes with a mixed co-ordination sphere. Thus, for example, the stepwise formation of thiocyanate complexes of iron represents essentially competition of the two ligands H_2O and SCN^- in the primary co-ordination sphere $[Fe(H_2O)_m(SCN)_{6-m}]^{(m-3)}$. The formation of such compounds is, however, still not typical of ternary complexes, since the properties such as absorption spectrum and redox potential can to a considerable extent be calculated by the laws of additivity.

At the same time thermodynamics do not prohibit the formation of a mixed co-ordination sphere with properties not governed by addivity. It is also in general possible for a ternary compound ABC to dissociate into species other than those from which it was formed:

$$2AB + 2C \rightleftharpoons 2ABC \rightleftharpoons AB_2 + AC_2. \quad (4)$$

The direction of reaction (4) depends on the properties of the central atom and ligands, on the solvent, *etc.*

The formation of stable ternary complexes is observed particularly often for high-valence elements. At the present time there are plenty of facts available about ternary compounds.[6] The properties of four of the most important groups of ternary complexes and their significance for analytical chemistry are examined briefly below.

SYSTEM METAL ION, ELECTRONEGATIVE LIGAND, ORGANIC BASE

Ternary compounds of this type are the most well-known and are widely used. A typical example has already been quoted—the copper–pyridine–salicylate system. Over a certain range of concentrations the equilibria in this system can be explained in terms of the triangular composition $[Cu^{2+}]$, [py], $[Sal^{2-}]$. If, as usual for fusion or solution systems, a property of the solution, *e.g.*, absorbance, is plotted perpendicular to the frame of the triangle, then a maximum on the surface indicates the formation of a ternary compound and gives its composition. In the case cited the compound can be examined[3] as a pseudo-binary complex in the systems $[Cu^{2+} . py_2]$–Sal^{2-} or [CuSal]–py in exactly the same way as for ternary fusion systems.

A more detailed study of similar systems for other metals and in wide ranges of concentration and pH shows that compounds with similar properties, but which differ structurally, can be formed. As a rule the formation of a series of intermediate compounds is observed, of which the extremes are, for example, the following: $[CuSal_2^{2-}] . 2[pyH^+]$, $[Cupy_2 . Sal_2^{2-}]$ and $[Cu . py_2 . Sal]$.[7] Certain compounds of this group are, according to their composition, similar to ion-association complexes. For the latter, however, additivity of properties (especially absorption spectra) is characteristic; and for the groups of compounds named the properties are characteristic and not additive, and the position of the equilibrium depends on the concentration of all three components.

The importance of this group of ternary complexes in analytical chemistry is very well-known, and therefore only brief mention of the basic applications is needed here.

Extractive photometric methods

These methods, for the determination of many cations which have inherent chromophoric properties, are based on the conjunction of an anionic metal complex with an onium cation or of an anion with a cationic metal complex. As an example, many metals form compounds of the type: metal ion–diantipyrilmethane–thiocyanate,[8] *e.g.*, titanium, vanadium, niobium, iron, cobalt.

If the co-ordination bonds of, *e.g.*, a metal–amine complex, predominate, ion-association compounds are mainly formed, in which the amine complex is the cation. The absorption spectrum of the ion-association compound is then similar to that of the metal–amine complex; *e.g.*, complexes of metals with dipyridyl.[9] On the other hand, if the co-ordination bond between the metal ion and the electronegative ligand is the stronger, then the ion-association compound is an onium salt of the anionic metal complex, *e.g.*, the compounds which form during the extraction of magnesium 8-hydroquinoline complexes in the presence of amines.[10] If the energies of the metal–amine and metal–electronegative ligand bonds are of the same order, then molecular compounds are formed, with a mixed co-ordination sphere. Examples are the pyridine–salicylate complexes mentioned earlier, or complexes of copper with EDTA and ammonia.[11] In such cases the absorption spectrum of the three-component system (ABC) often differs from the spectra of the separate binary combinations AB and AC.

Photometric and fluorimetric methods

The compounds of anionic metal complexes and basic dyes have great importance for photometric determination of metals which do not have inherent chromophore properties. For example, the most important development in the photometric determination of antimony is based on the formation of ion-association complexes of basic dyes with anionic antimony chloro-complexes.[12–14] Very useful methods for borate and tantalum are based on extraction of the basic dye–fluorocomplex into benzene.[15–17] Similar methods have been described for thallium,[18] gold,[19] gallium[20] and other elements.[21] The three component reaction system is the general basis of these methods; the binary combinations metal–halide and dye–halide are also possible: the choice of organic extractant and concentration conditions are of great importance, because the dye–halide combination must not be extracted along with the ternary compound.

Extractive ion-exchange systems

The reaction between anionic metal complexes and high molecular weight organic bases is very important for the separation of many metals by means of anion-exchange resins or so-called "liquid ion-exchangers". In the latter method the anionic complex is extracted with a solution of a high molecular weight amine in an inert solvent. The extraction method is very widely used; a typical review[22] covers hundreds of papers. An examination of the methods from a general point of view, based on the formation of ternary complexes, allows us to establish a series of general principles and to transfer to extraction systems the methods worked out for ion-exchange, and *vice versa.*

The methods based on the interaction of anionic metal complexes with organic compounds containing oxygen, such as tributyl phosphate, high molecular weight alcohols, *etc.*, are also similar to this group of reactions. A typical example is the formation of coloured compounds between alcohol and vanadium 8-hydroxyquinolate.[23,24] The bonds between anionic metal complexes and organic compounds containing oxygen are relatively weak, so the spatial accessibility of the oxygen atom of the auxiliary ligand molecule assumes special importance.[25]

Finally, the chemical reactions and extractional equilibria in these systems are important when the systems are used for determining the auxiliary ligand instead of the central metal ion. Thus, many of the important methods for determining alkaloids or for separating a mixture of high molecular weight bases are founded on similar reactions with anionic metal complexes. It is not the character of the chemical equilibrium that is the main difference but the requirements for the choice of organic solvent and conditions of acidity.

SYSTEM METAL ION, TWO DIFFERENT ELECTRONEGATIVE LIGANDS

Some of these systems have been known for a long time and are mentioned in monographs on the chemistry of complex compounds. Thus, for example, in the system Fe^{3+}–SCN^-–Hal^-, compounds containing both ligands are found.[26] They are conveniently called mixed-ligand complexes. The change in absorbance, measured on a filter-type instrument, is not much different from that which can be calculated,[3] on the basis of the reaction

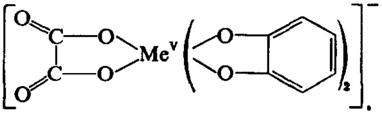
$$Fe(SCN)_m^{3-m} + nCl^- \rightleftharpoons FeCl_n^{3-n} + mSCN^-. \qquad (5)$$

Such equivalence of some substitution systems and ternary complex systems permits the use of the former as simpler equilibrium models. However, the absorption spectra show that in the case cited no simple decrease occurs in the intensity of the band characteristic for iron(III)–thiocyanate complexes, during the simultaneous intensification of the band corresponding to iron(III)–chloride complexes. In fact there is a departure from additivity, with a shift in the position of the maximum.

In many other reactions, especially with high-valence metals the departures from additivity are even more noticeable. Here the absorption spectrum of the system M–X–Y often differs sharply from any possible combinations of spectra of M–X and M–Y.

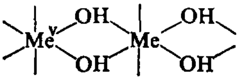
In general there has been little work done on the equilibrium chemistry of complexes of high-valence elements. In fact, the number of reactions for which the thermodynamic equilibrium constants are known is roughly inversely proportional to the square of the oxidation state of the cations concerned. Such a numeration process, however, does not provide reasons why the situation exists. The reasons lie mainly in the special features of the chemistry of high-valence elements and in the more complicated procedures of study consequently demanded, the two chief reasons being the formation of polymeric hydroxo-complexes, which drastically reduces the reactivity of these elements (*cf.* the review[27]), and the formation of ternary complexes with properties differing from those of any of the binary compounds in the systems M–X and M–Y.

Patrovský[28] was probably the first to notice this feature, in his studies on niobium. It is known that EDTA usually destroys coloured metal complexes, binding the metal ion in the more stable EDTA-complexes. However, if EDTA is introduced into a solution of the *o*-dihydroxybenzene–niobium complex, the colour becomes stronger. Detailed research on coloured complexes of tantalum and niobium with *o*-dihydroxybenzene (and pyrogallol *etc.*) shows that these reactions are connected with the formation of ternary complexes.[29] Thus, for example, complexes of tantalum with either *o*-dihydroxybenzene or oxalic acid absorb only in the ultraviolet, but if both ligands are added together a yellow complex is formed of the type



The pyrogallol method for photometric determination of tantalum in acid medium is also founded on the formation of a ternary complex. No attention was usually paid to this because in the procedure used, tantalum and niobium pentoxides were fused with alkali or pyrosulphate, and the cooled melt was dissolved in water containing tartaric or oxalic acid to prevent precipitation of the metal hydroxides. It has now been established that these acids also play the role of auxiliary ligand during the formation of the coloured complexes.

Not long ago niobium and tantalum were still thought of as elements which scarcely reacted with the usual metallochromic indicators. However, in recent years it has been made clear[30-34] that niobium and tantalum form coloured complexes with various metallochromic indicators, and not only when "activators" such as hydrogen peroxide, EDTA, oxalic or tartaric acid, are introduced. On the other hand, these "activators' often destroy the coloured complexes of many bivalent and tervalent metals. However, for niobium(V) and tantalum(V) these reagents play the role of auxiliary complex formers which destroy the polynuclear hydroxo-complexes of these quinquevalent metals. The activators usually prove to be small complexing agents; they are therefore kinetically beneficial because they quickly destroy the bonds in the polymeric chains of the type:



Metallochromic indicators, HInd, contain complex-forming groups, but on account of the large size of the HInd molecule the rate of reaction with polymeric niobium or tantalum species is very low. Heating speeds up this reaction, but the hydrolysis is accelerated even more, and so is the almost irreversible process of dehydration of the polynuclear hydroxo-complexes. The role of the auxiliary ligand is, however, not limited to the destruction of the polynuclear species, otherwise only colourless complexes of ML_n would be obtained, where M denotes the metal ion. On account of the spatial characteristics (as yet less often studied) of high-valence ions and various types of ligand, a coloured ternary complex compound MLInd is formed. Gradual displacement of the metallochromic indicator by the auxiliary ligand is observed only with ligands which form very strong M–L bonds (*e.g.*, fluoride) or with a very large excess of the ligand.[31]

It would be inconvenient to examine in detail the extensive literature on the analytical chemistry of niobium and tantalum, and of other high-valence elements. Only some general characteristics can be noted. When silver chloride is dissolved in ammonia or potassium cyanide, the reaction is a simple displacement, the soluble complex forming immediately. For high-valence metals, however, the situation is different. The action of fluoride or oxalate on zirconium, niobium or tantalum hydroxide is more complicated. The ligand is often initially incorporated into the solid phase, forming a compound even less soluble than the initial hydroxide. Soluble complexes form only when there is a large excess of the ligand or the acidity conditions are favourable. In both cases the compounds which form contain two ligands—the hydroxyl ion and the added ligand.

The importance of ternary complexes can also be seen from consideration of the history of the many attempts to work out methods for complexometric titration of titanium. A satisfactory solution was found only when an auxiliary complex-former—hydrogen peroxide—was introduced. Many other examples can be quoted of the formation of ternary complexes containing the metal ion and two different electronegative ligands. Thus, the uranyl ion is precipitated by the action of hydrogen peroxide in alkaline medium, and it forms a weakly coloured complex with carbonate; use of both peroxide *and* carbonate results in a soluble coloured compound. This reaction is the basis of one of the best known methods for photometric determination of uranium. The analytical chemistry of high-valence elements can develop only if attention is paid to the formation of ternary complexes.

Similar ternary complexes probably are important in many catalytic reactions, acting therein as charge transfer complexes, the metal ion assisting the migration of an electron from the one ligand to the other.

TERNARY HETEROPOLY COMPLEXES

Methods of analysis based on the formation of heteropoly acids are very important, and for the determination of small quantities of certain elements, such as phosphorus or silicon, it is impossible to use any other methods. Similar compounds are also important in the determination of arsenic, germanium and other elements. Many heteropoly acids form slightly soluble salts with alkaloids and other organic bases. The unusual composition of these compounds long ago attracted the attention of chemists. As yet the co-ordination of 12 molybdenum atoms around one small hetero-atom (phosphorus, *etc.*) has not been completely settled. It is known that 4 oxygen atoms are distributed tetrahedrally around the central hetero-atom, and that two molybdenum atoms are associated with each edge of the tetrahedron, but the structural differences between the so-called α and β forms[35] of the heteropoly acids have not yet been elucidated, though suggestions have been made.[36] It may be noted in passing that the tendency to form heteropoly acids decreases with increase in size of the central hetero-atom. Thus, antimony, tantalum and bismuth do not form such complex compounds although they have *d*-electrons and in general are more inclined to form complexes than are silicon and phosphorus.

It is known from X-ray work that the co-ordination number of phosphorus in phosphomolybdic acid is 4, so if the molybdenum is regarded as forming trimeric groups the formula is written $H_3P(Mo_3O_{10})_4$. However, these facts, like many others about the structure of solid substances, do little to explain the properties of compounds in solution. First of all, the study of the structure of sexivalent molybdenum species in solution does not verify the formation of trimers. The X-ray work shows that each molybdenum atom is co-ordinated to 6 oxygen atoms and that the central PO_4 group is an integral and necessary part of the structure. Next, the X-ray evidence does not explain why one phosphorus atom essentially changes the optical properties of all 12 molybdenum atoms; the absorption spectrum of the phosphomolybdate is determined by the shift of the absorption band of molybdate. Further, a significant change in the properties is apparent; ammonium phosphate and molybdate are, separately, highly soluble in water, whereas ammonium phosphomolybdate is but slightly soluble. Finally, a strong chemical interaction between the central atom and the molybdate is corroborated by the great difference in stability of the phosphorus, silicon and arsenic compounds. X-Ray data give the arrangement of the atoms in the crystal lattice, but do not explain the character of the chemical bond between the components of the complex.

It is known[37] that the formation of phosphomolybdic acid is very far from being complete unless the equilibrium is shifted by removal of the product either by reduction or further complexation with, *e.g.*, acetone. Therefore it might be expected that any species able to bind phosphate or molybdate would destroy phosphomolybdic acid. Thus it would come as no surprise if the addition of niobium to a phosphomolybdate led to its decomposition with the formation of a slightly soluble niobium phosphate or molybdate. On the contrary, however, a ternary niobium–phosphate–molybdate complex[38,39] is formed. A similar process occurs in the phosphate–molybdate–vanadate systems,[40–42] and phosphate–titanium–molybdate[43] systems, *etc.* These complexes absorb light more intensely than the simple phosphomolybdic acid in the visible part of the spectrum. These ternary heteropoly acids are also characterized by stability over a wider pH range and for their complete formation a smaller excess of molybdate is needed. The individuality of such complexes is verified by the fact that they can be separated from phosphomolybdic acid by extracting the latter with butanol.

The use of such ternary complexes in analysis is of interest because of their high specificity for titanium and niobium determination.

SYSTEM ONE LIGAND, TWO DIFFERENT METALS

Compounds of this group have been much less studied, because of experimental difficulties. Nevertheless there is no doubt that they are often formed. No fewer than three sub-groups of such ternary complexes can be noted: (*a*) polymeric groups in which two different metals are bound through an oxygen atom or bound by chelating reagents, with the chelate groups considerably distant from each other, (*b*) compounds containing two atoms of one metal in different oxidation states, and (*c*) compounds containing the so-called "outer-zone bond", in which the properties of the metal inside the co-ordination zone depend on the nature of the metal outside the co-ordination zone.

The existence and importance of the first sub-group are very well-known. Thus, in the analytical chemistry of tantalum, niobium and titanium there are well-known facts for which the term "loss of individuality" is used. This phenomenon consists of the fact that the behaviour of the elements is different when they occur together from what it is when they occur separately, which greatly hinders their separation.[44–46] The reason for "the loss of individuality" seems likely to be as follows. Study of the rate of dialysis and other properties of the ions of the high-valence elements shows, for example, that in a chloride solution niobium exists as monomeric species only at concentrations of hydrochloric acid $>10M$,[47] and that tantalum occurs as polynuclear hydroxo-complexes even in concentrated hydrochloric acid.[48] The reactivity of tantalum and niobium is sharply reduced in the absence of auxiliary complexing agents.[49] The state and reactivity of many high-valence elements change drastically with the age of the solutions. If a mixture of solutions of such elements is allowed to stand, polynuclear hydroxo- and oxo-complexes form, containing more than one element, catenated by the oxygen atoms.

It is known[50] that in the presence of tantalum the formation of the coloured niobium thiocyanate complex is incomplete; however, if the polymeric tantalum species are added to a solution of niobium thiocyanate prepared in advance, the colour does not diminish.

In some cases the formation of mixed polynuclear species can prove useful. Zirconium, for example, reacts feebly with metallochromic indicators if an initially strongly acid solution is neutralized with ammonia, and then adjusted with acid to the optimum pH. This effect can be eliminated by addition of aluminium salts before neutralization of the solution.[51] Apparently in the first case inert polynuclear zirconium species form, the M—O—M bonds in which are only slowly broken by the protons added; in the presence of aluminium mixed polymers form, containing chains of Al—O—Zr units, the bonds in which are more readily attacked by protons.

The formation of polynuclear species of high-valence elements is important not only for aqueous solutions, but also for solutions in anhydrous acetic acid.[52]

Probably similar structures and properties are to be found in complexes of metals with organic reagents in which the chelating groups are located far away from each other. Such reagents are widely used and research is being done on them,[53,54] although the reaction mechanism and the character of the compounds has so far been but little studied. It has been repeatedly noted, that for spatial reasons a single metal atom cannot form a chelate with all the bonding groups of a reagent if these are too far separated, as for example, in Methylthymol Blue, even though they are as strongly complex-forming as the iminodiacetic acid group.[55] A high-valence element can bind the separate "ends" of two molecules of a chelate reagent, forming a chelate polymer.[56] The formation of such polymers has been shown for Methylthymol Blue.[57] The inclusion of different metals in one chain is also possible, *i.e.*, the formation of ternary complexes. According to the findings from the absorption spectra, similar phenomena are observed even for tartrate complexes, since the molecule of tartaric acid can bind two metals separately through its pairs of carboxyl and hydroxyl groups. Thus, it is known[58] that the absorption spectrum of a copper tartrate complex changes in the presence of aluminium.

A similar effect is observed for the system magnesium, Titan Yellow, iron(III). The addition of tartrate does not hinder the magnesium reaction with Titan Yellow, and iron(III) in the presence of tartrate does not itself react with Titan Yellow. However, if Titan Yellow and alkali are added to a mixture of magnesium, iron and tartrate, the reaction with magnesium is not observed.[59]

Several instances of formation of ternary complexes of one ligand with different metals are well-known, particularly for many reactions of tin(II). It is known that iron(III) dimethylglyoximate obtained in the usual conditions decomposes at pH <4. However, if tin(II) is introduced during the formation of this complex, a more stable complex forms which has a different absorption spectrum. Tin(II) alone does not form complexes with dimethylglyoxime in the given conditions, and tin is not precipitated from the ternary complex even by hydrogen sulphide[60] A similar ternary complex forms during the interaction of tin(II), molybdenum and dimethylglyoxime,[61] and also in the corresponding rhenium system.[62]

Ternary complexes containing two different oxidation states of one metal are very interesting in photometric analysis. It is known that such compounds are usually intensely coloured, *e.g.*, Prussian blue and molybdenum blue. This property was reported long ago in the first works on the colour theory of inorganic compounds.[63,64] The high colour of such compounds was explained by the ready oscillation of an electron between two identical atoms in the same molecule ("inorganic quinhydrones"). Nowadays, this is explained by the fact that within the boundaries of the one molecule the ionization potential of the lower oxidation state is almost equal to the electron affinity of the higher oxidation state. Therefore the electron is easily transferred even by low energy quanta in the visible part of the spectrum.[65] It is also known that a mixture of ter- and quadrivalent titanium in a solution is of a more intense colour than tervalent titanium alone. There are also reports of non-additivity of the absorption spectra of a mixture of chlorides of ter- and quinquevalent antimony,[66] bi- and quadrivalent tin,[67] and bi- and quadrivalent palladium.[68]

Finally, during photometric determinations, and even during separations by extraction, there may be a significant influence of metals which apparently do not enter the co-ordination zone, *i.e.*, they do not form complexes under the given conditions, but they influence the absorption spectra and the reactivity of the other complexes. Many of the recorded facts show that this influence is specific and in no way can it be considered as due to changes in the ionic strength of the solution. Thus the extraction of a thiocyanate complex of iron changes remarkably according to which of the univalent alkaline metals is used in the base electrolyte.[69] Further, in the thiocyanate method for molybdenum, any iron(III) is reduced, and though bivalent iron does not itself react with thiocyanate the absorption spectrum of the molybdenum thiocyanate complex is noticeably changed in the presence of bivalent iron,[70] and also in the presence of some other ions.

Résumé—Les réactions entre un complexe AB et un troisième constituant C ne procèdent pas toujours par un mécanisme de déplacement régi par la différence d'énergie des liasons chimiques A—B et A—C. Le troisième constituant devient souvent partie du complexe, formant une sphère de coordination mixte ou un complexe ternaire. Les propriétés de ce complexe ternaire ABC ne sont pas des fonctions additives des propriétés de AB et AC. De telles réactions sont importantes dans de nombreuses méthodes en chimie analytique, particulièrement en analyse photométrique, séparation par extraction, dissimulation, etc... On passe en revue les propriétés générales des quatre types fondamentaux de complexes ternaires et donne des exemples. Les quatre types comprennent les systèmes (a) ion métallique, ligand électronégatif, base organique, (b) un ion métallique, deux ligands électronégatifs différents, (c) hétéropolyacides ternaires et (d) deux ions métalliques différents, un ligand.

Zusammenfassung—Reaktionen zwischen einem Komplex AB und einer dritten Komponente C verlaufen nicht immer über eine Verdrängungs-reaktion, die durch die Energiedifferenz der Bindungen A—B und A—C beherrscht wird. Oft wird die dritte Komponente ein Teil des Komplexes: es bildet sich eine gemischte Koordinationssphäre oder ein ternärer Komplex. Die Eigenschaften dieses ternären Komplexes ABC sind keine additiven Funktionen der Eigenschaften von AB und AC. Solche Reaktionen sind bei vielen Methoden der analytischen Chemie wichtig, besonders bei der photometrischen Analyse, der extraktiven Trennung, der Maskierung usw. Es wird eine Übersicht über die allgemeinen Eigenschaften der vier Grundtypen ternärer Komplexe gegeben und Beispiele vorgestellt. Die vier Typen umfassen die Systeme: (a) Metallion, elektronegativer Ligand, organische Base; (b) ein Metallion, zwei verschiedene elektronegative Liganden; (c) ternäre Heteropolysäuren; (d) zwei verschiedene Metallionen, ein Ligand.

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DETERMINATION OF IRON, NICKEL, CHROMIUM AND VANADIUM BY MEANS OF REDOX AND ION-EXCHANGE COLUMNS

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Summary—Redox and anion-exchange columns have been used to separate and determine iron, nickel, chromium and vanadium in solution. The anion-exchange columns provide some of the separations, and the redox columns are used for the determination of the iron, chromium and vanadium. The chromium and vanadium may be determined in the presence of the iron by adjustment of the acidity in the redox column. By using a column "memory" technique, titration of the actual metal solution has been avoided. The method shows some advantages over conventional methods.

INVESTIGATIONS into the formation of corrosion deposits on probes inserted into oil-fired furnaces in power-stations resulted in a need for simple methods of analysis of mixtures of metals occurring in steels and fuel-oils. Typical metals occurring in such deposits are iron, chromium and nickel from the probe-steel, and vanadium and sodium from the fuel-oil. Previous studies[1] on the use of redox reactions on columns for the analysis of metals occurring in more than one oxidation state suggested that, used in conjunction with ion-exchange columns, such columns could give simple and effective separations and determinations.

The redox columns consist of tetrachlorohydroquinone deposited on a suitable inert substrate such as diatomaceous earth. Passage of an iron(III) solution at a suitable pH results in reduction to iron(II) plus the formation of an equivalent amount of the oxidized form, tetrachloroquinone, of the redox compound. This tetrachloroquinone acts as a "memory" of the iron(III) that has passed through the column, and reduction with excess of ascorbic acid followed by a back-titration with iodine solution provides a measure of the amount of iron passed. Because the iron solution itself is not titrated, titration difficulties due to the presence of other metals are avoided. As the potentials of redox couples depend on pH and concentrations of complexing species, a certain degree of flexibility is provided; *e.g.*, iron(III) is reduced to iron(II) in $0{\cdot}03M$ hydrochloric acid but not in $2M$ hydrochloric acid (complex formation effect), whereas vanadium(V) and chromium(VI) are reduced to vanadium(IV) and chromium(III) respectively in $2M$ hydrochloric acid (pH effect).

The anion-exchange separations used in this paper have been described by Kraus and Nelson.[2] In chloride media, the chloride complexes and oxy-anions formed by metals are adsorbed on to anion-exchange resins to varying degrees according to the concentration of chloride ions present. Thus these authors report that alkali metals, alkaline earths, aluminium(III) and nickel(II) are not adsorbed even in the presence of $12M$ hydrochloric acid; vanadium(IV), chromium(III) and manganese(II) are slightly adsorbed from a $12M$ hydrochloric acid medium; iron(II) and vanadium(V) are adsorbed but eluted when the medium is diluted to $7M$ hydrochloric acid, and iron(III) is eluted by $1M$ hydrochloric acid. Chromium(VI) in the form of the oxy-anion is very strongly adsorbed and difficult to remove in chloride media.

The two types of column (redox and ion-exchange) have therefore been used to determine the composition of a solution containing iron(III), vanadium(V), chromium(VI) and nickel(II).

EXPERIMENTAL

Materials

Amberlite Resin CG 400, 100–200 mesh, B.D.H. Ltd.
Celite A, 80–120 mesh, B.D.H. Ltd.
Tetrachlorohydroquinone, Eastman Organic Chemicals, (Kodak Ltd.).

Preparation of redox columns

Tetrachlorohydroquinone (1·5–2 g) was deposited on 5 g of diatomaceous earth (Celite A) from ethereal solution.[1,3] To the paste obtained after evaporation of most of the ether were added successive quantities of 0·03*M* hydrochloric acid until a smooth slurry was obtained. This slurry was poured into a 1-cm diameter glass column fitted with a sintered disc (porosity 0) and tap, the resulting redox column being about 10 cm long.

Preparation of anion-exchange columns

Amberlite Resin CG 400, 100–200 mesh, was washed several times with distilled water and decanted to remove the fines. A column 5 cm in length was prepared by pouring the aqueous slurry into a column of 2-cm bore glass tubing into the bottom end of which was sealed a sintered glass disc of porosity 3. The column was conditioned by washing six times with a cycle of 2*M* sodium hydroxide, water, 2*M* hydrochloric acid and water.

Neither type of column was allowed to run dry as this would allow air-bubbles to collect in the beds and slow the flow-rates. The columns were always conditioned before use by passage of 20–25 ml of the appropriate solvent (0·03*M* hydrochloric acid or water) used in the test solution. The columns were also washed through after the passage of the test solution.

Preparation of solutions of corrosion deposits

Corrosion deposits may be dissolved by several standard methods, *e.g.*, 1 g of finely ground deposit is mixed with 5 g of 100:15 w/w sodium carbonate/borax mixture and fused in a platinum crucible. The product is then dissolved in sulphuric acid.

Saltzmann[4] has described a method for the oxidation of the metals to their highest oxidation states. After oxidation with potassium permanganate in dilute sulphuric acid, the excess of permanganate is destroyed with 2% sodium azide solution.

Recommended procedure

The principles of the method are outlined diagrammatically in Fig. 1. Vanadium and chromium were first determined together after passage of 20 ml of solution A (plus sufficient concentrated hydrochloric acid to give a 2*M* solution) down a redox column, and washing through with 2*M* hydrochloric acid followed by distilled water. A flow-rate of approximately 30 ml/hr was used, care being taken that the column capacity was sufficiently high. This could be checked visually by observing the extent of the yellow band of tetrachloroquinone in the column. This tetrachloroquinone, equivalent to the vanadium(V) and chromium(VI), was then reduced by passing through the column an excess (20 ml) of 0·1*N* ascorbic acid and washing it through with 20–30 ml of distilled water. The unreacted ascorbic acid was back-titrated with 0·1*N* iodine solution, with starch as indicator.

Chromium(VI) was then removed from 60 ml of solution A (made 0·5*M* in hydrochloric acid) by passing it down anion-exchange column I and washing it with 0·5*M* hydrochloric acid. The effluent was made up to 100 ml (solution B), 20 ml of which were made 2*M* in hydrochloric acid and passed down a redox column to determine the amount of vanadium(V) present.

The nickel was obtained free from interfering metals by passing 20 ml of solution B (made 8*M* in hydrochloric acid) down anion-exchange column II. The nickel passed through unadsorbed, and a further 20–30 ml of 8*M* hydrochloric acid were passed through to ensure complete removal of the nickel. The nickel was then determined gravimetrically with dimethylglyoxime. It should be noted that anion-exchange columns that have been used to remove chromium should not be used for nickel removal because the 8*M* hydrochloric acid would reduce the adsorbed chromium(VI) to chromium(III) and then elute it, thereby contaminating the nickel.

After the nickel removal, 20–30 ml of 4*M* hydrochloric acid were passed through column II to remove the vanadium, and this effluent was discarded because a certain amount had also emerged in the nickel solution.

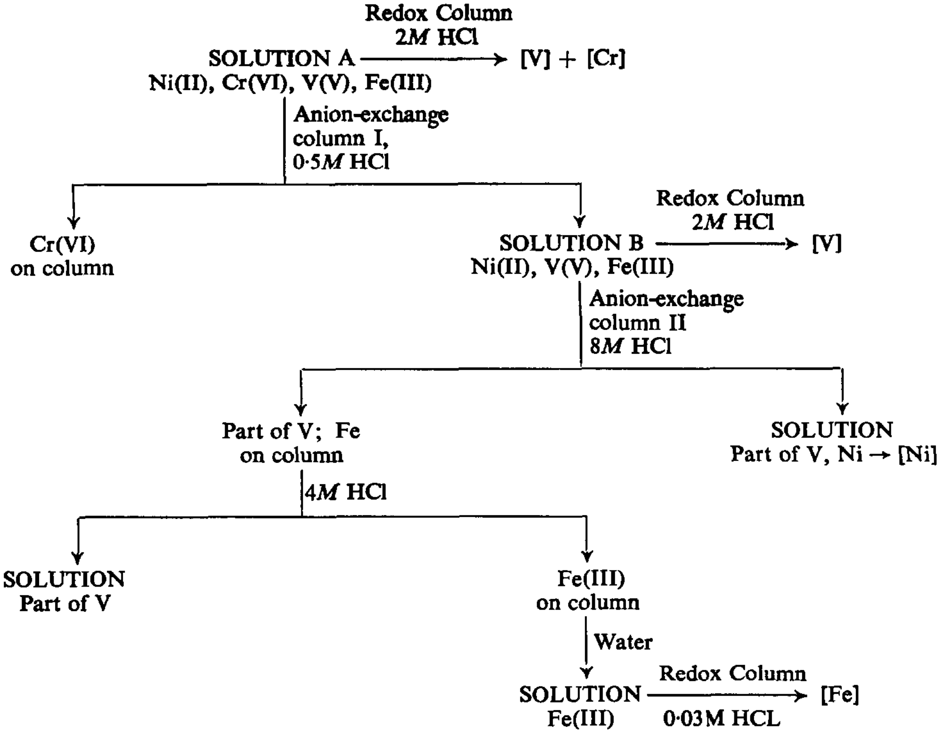

FIG. 1.—Separation and determination of Ni(II), Cr(VI), V(V) and Fe(III).

The iron was obtained by passing 20–30 ml of water down column II. Collection was started as soon as the yellow colour of the iron(III) chloro-complex appeared through the column sinter. For the purpose of determining the iron(III) concentration on a redox column it was essential that the acidity should not exceed 0·03*M*. Accordingly, the iron eluate was made slightly alkaline with dilute ammonia and then the brown gelatinous precipitate was just redissolved with dilute hydrochloric acid so that the final acidity did not exceed 0·03*M*. The iron content was then determined by passing the solution through a redox column (conditioned with 0·03*M* hydrochloric acid) followed by reduction with ascorbic acid and back-titration with iodine solution.

RESULTS AND DISCUSSION

Ion-exchange column behaviour

Nickel. A solution of nickel chloride in concentrated hydrochloric acid was passed through the column; the eluate was shown to contain nickel. Elution of the column with 0·5*M* hydrochloric acid gave no further nickel in the eluate, *i.e.*, nickel was not adsorbed on the column.

Chromium. Passage of a solution of potassium dichromate in 0·5*M* hydrochloric acid resulted in the complete adsorption of chromium(VI). This could only be eluted with concentrated hydrochloric acid, which slowly reduced it to chromium(III) which was then eluted.

Vanadium. Kraus and Nelson[2] reported that vanadium(V) is adsorbed from concentrated hydrochloric acid solutions and eluted by 7*M* hydrochloric acid. The hydrochloric acid concentration of the sample solution, which after passage down column I is 0·5*M*, must therefore be increased and this could be achieved by saturation with hydrochloric acid gas. A more convenient alternative was sought by adding concentrated hydrochloric acid ($11M$) to the sample solution. A $10M$ acid concentration requires the addition of 100 ml of concentrated acid to 10 ml of sample solution but this large total volume, besides being inconvenient to handle, appeared to cause the elution of the vanadium (see Table I). Therefore a lower concentration of $8M$ was chosen because this gave adsorption of all but a trace of the vanadium with the minimal addition of hydrochloric acid. An interesting observation was made during the subsequent elution of the vanadium from the column. The use of $7M$ hydrochloric acid gave a blue eluate of vanadium(IV) whereas $4M$ acid gave a yellow eluate of vanadium(V). A similar observation had been made with chromium in the previous section where the passage of concentrated hydrochloric acid led to the reduction of chromium(VI) to chromium(III). Strelow and Bothma[5] also noted the reduction of chromium(VI) on a anion-exchange column and ascribed it to reduction by the quaternary ammonium resin.

TABLE I.—SEPARATION OF NICKEL, VANADIUM AND IRON BY ANION-EXCHANGE

Sample volume, *ml*	10	5	7·5
Conc. HCl added, *ml*	100	22·5	20
Resultant [HCl], *M*	10	9	8
Metals eluted: *a*, immediately	Ni, V*	Ni, V (trace)	Ni, V (trace)
b, by $4M$ HCl	None	V	V
c, by $0{\cdot}5M$ HCl	Fe	Fe	Fe

* Elution of vanadium probably due to large volume of hydrochloric acid used.

Iron. When solutions of iron(III) chloride in concentrated hydrochloric acid and in $4M$ hydrochloric acid were passed down a column there was no elution of iron(III) that could be detected by the addition of ammonium thiocyanate. The addition of $0{\cdot}5M$ hydrochloric acid or water eluted all of the iron absorbed on the column.

Separation and determination of nickel(II), chromium(VI), vanadium(V) and iron(III)

The information obtained was used to devise a scheme for separating the four metals. Solution A was prepared by mixing 50-ml quantities of $0{\cdot}1M$ nickel chloride, $0{\cdot}05M$ potassium dichromate, $0{\cdot}1M$ ammonium vanadate and $0{\cdot}1M$ iron(III) chloride and diluting to 250 ml with water.

Then 25 ml of this solution were made $0{\cdot}5M$ in hydrochloric acid and passed down a column. The first 10 ml of eluate were discarded as being the hold-up volume. The chromium(VI) was adsorbed as an orange layer. The column was washed with $0{\cdot}5M$ hydrochloric acid until the effluent was colourless. This eluate (total volume 30 ml) contained nickel, vanadium and iron, and was divided into three parts for passage down a second column at varying hydrochloric acid concentrations. The details and results are given in Table I. Some vanadium passes through with the nickel, but does not interfere with the subsequent determination with dimethylglyoxime.

These separation techniques were then combined with use of redox columns to determine the amounts of the four metals in Solution A. It has previously been reported[1,3] that iron(III) in $0{\cdot}03M$ hydrochloric acid is completely reduced by a redox column but not at all in $2M$ hydrochloric acid, and that vanadium(V) and chromium(VI) are completely reduced in 2*M* hydrochloric acid. However, no information was available for vanadium in 0·03*M* hydrochloric acid. A check experiment showed that ammonium vanadate is 40% reduced by passage down a redox column in 0·03*M* hydrochloric acid, and so, for the determination of iron, it is essential that vanadium is absent.

When solution A (made 2*M* in hydrochloric acid) was passed down a redox column, the recovery of vanadium(V) plus chromium(VI) was 0·0790–0·0848 mequiv/ml, average 0·0806, expected value 0·0800.

Table II gives results obtained for the determination of vanadium(V) after the removal of chromium(VI) by the anion-exchange column I. These showed that a concentration of at least 0·5*M* hydrochloric acid was necessary in the chromium removal step. Lower concentrations of chloride ion gave higher apparent vanadium values, *i.e.*, not all of the chromium was being removed.

TABLE II.—DETERMINATION OF VANADIUM AFTER REMOVAL OF CHROMIUM

HCl concentration used in chromium removal, *M*	Vanadium, *mequiv/ml*	
	Found	Taken
0·03	$0{\cdot}023_5$	0·020
	$0{\cdot}023_5$	
	$0{\cdot}022_5$	
	0·024	
0·2	$0{\cdot}021_5$	0·020
	0·021	
	0·022	
0·5	0·020	0·020
	0·020	
	0·020	

Nickel recovery, after removal of chromium(VI) with an anion-exchange column and 0·5*M* hydrochloric acid and of vanadium(V) and iron(III) with the second anion-exchange column and 8*M* hydrochloric acid, ranged from 100 to 106%, average 103%. Iron(III) recovery by final elution with water from the second anion-exchange column was 98%.

As a further check, four solutions containing various proportions of the four metals were analysed. The results obtained are given in Table III.

TABLE III.—ANALYSIS OF MIXTURES OF IRON, NICKEL, CHROMIUM AND VANADIUM

Metal	Solution I		Solution II		Solution III		Solution IV	
	Taken*	Found*	Taken*	Found*	Taken*	Found*	Taken*	Found*
Iron	0·0833	0·0838	0·0313	0·0321	0·1459	0·1483	0·0313	0·0332
Nickel	0·0344	0·0339	0·0917	0·0923	0·0344	0·0339	0·0573	0·0581
Chromium	0·0104	0·0107	0·0312	0·0318	0·0104	0·0109	0·0416	0·0409
Vanadium	0·0611	0·0616	0·0204	0·0196	0·0204	0·0196	0·0815	0·0818

* In g/100 ml of solution.

Zusammenfassung—Zur Trennung und Bestimmung von Eisen, Nickel, Chrom und Vanadium in Lösung wurden Redox- und Anionenaustauschsäulen verwendet. Die Anionenaustauschsäulen ermöglichen einige der Trennungen, die Redoxsäulen werden zur Bestimmung von Eisen, Chrom und Vanadium gebraucht. Chrom und Vanadium können neben Eisen durch Kontrolle der Acidität in der Redoxsäule bestimmt werden. Durch Verwendung eines Speicher-(“memory”)-verfahrens in der Säule wurde die Titration der Metallösung vermieden. Die Methode zeigt Vorteile gegenüber bisher bekannten Verfahren.

Résumé—On a utilisé des colonnes redox et échangeuses d’anions pour séparer et déterminer le fer, le nickel, le chrome et le vanadium en solution. Les colonnes échangeuses d’anions fournissent quelques-unes des séparations et l’on utilise les colonnes redox pour la détermination du fer, du chrome et du vanadium. On peut déterminer le chrome et le vanadium en présence du fer par ajustage de l’acidité dans la colonne redox. En utilisant une technique de colonne “à mémoire”, on a évité le titrage de la solution réelle de métal. La méthode montre quelques avantages par rapport aux méthodes ordinaires.

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DETERMINATION OF HYDROGEN PEROXIDE BY XENON TRIOXIDE OXIDATION

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Summary—Aqueous xenon trioxide solution has been used as the oxidizing agent in three precise methods of analysis for hydrogen peroxide. A catalytic method, which utilizes hydrogen peroxide to initiate the reaction between t-butanol and xenon trioxide, is described for determining amounts of hydrogen peroxide as low as 0.9 μg or 36 parts per milliard (ppM). A direct spectrophotometric titration was found to have a lower limit of about 50 μg or 20 ppM. An indirect titrimetric method was also used to determine hydrogen peroxide in amounts as low as 50 μg with a relative standard deviation of 4% which decreased to 1% for amounts over 200 μg.

XENON trioxide has previously been proposed for the determination of primary and secondary alcohols[1] and certain organic acids.[2] Aqueous solutions of xenon trioxide ("xenic acid") are strong oxidizing agents. Appelman and Malm[3] have estimated the redox potential of the Xe(VI)–Xe(O) couple to be about +1·8 V in acidic and +0·9 V in basic solution. It will oxidize ammonia to nitrogen, hydrogen peroxide to oxygen, chloride to chlorine and manganese(II) to permanganate. Xenic acid also reacts readily with *vic*-diols to yield carbon dioxide and xenon.[4]

Aqueous solutions of hydrogen peroxide in acid media are usually determined by titration with potassium permanganate[5] or cerium(IV),[6] or iodometrically[7] with ammonium molybdate as catalyst. Recently the direct titration of hydrogen peroxide in alkaline bromide media has been accomplished with sodium hypochlorite.[8]

Aqueous xenon trioxide solution may also be used to determine hydrogen peroxide. A catalytic method, a direct spectrophotometric titration, and an indirect titration method are described for determining amounts of hydrogen peroxide as low as 36 parts per milliard (ppM).

EXPERIMENTAL

Apparatus

The change in absorbance of xenon trioxide at 200 mμ was measured with a Cary Model 14 spectrophotometer. Matched quartz cells of 1-cm optical path were used. A Beckman Expanded Scale pH Meter equipped with a saturated calomel and glass electrode was used for all pH measurements.

Reagents

Xenon trioxide standard solution was prepared by the hydrolysis of xenon hexafluoride.[9] Since the hydrolysis by-product, hydrofluoric acid, did not interfere in the reaction, no attempt was made

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to remove it from the standard solution. Reagent grade chemicals were used without further purification. *t*-Butanol was purified by distillation. The hydrogen peroxide was standardized against sodium iodide, ammonium molybdate being used to catalyse the reaction. Standard sodium thiosulphate was used for the titration of the tri-iodide resulting from this oxidation. This solution was also used to titrate the iodine from the oxidation of iodide by the xenon trioxide. A 5-ml semi-micro burette was used for all titrations.

Procedure

The catalytic method employed a solution of hydrogen peroxide, *t*-butanol and phosphate buffer in one beaker; xenon trioxide was added to a second beaker. Hydrogen peroxide catalysed the reaction between *t*-butanol and xenon trioxide. Equal amounts of potassium dihydrogen phosphate and potassium monohydrogen phosphate ($8 \times 10^{-3}M$) were added to buffer the solution to pH 7. The hydrogen peroxide concentration was varied from $1 \times 10^{-6}M$ to $5 \times 10^{-5}M$; the initial xenon trioxide and *t*-butanol concentrations were held constant at $2{\cdot}7 \times 10^{-4}M$, and $1 \times 10^{-4}M$ respectively. The volume of solution in each beaker was either 10 or 15 ml, so that on mixing, the total volume was exactly 25 ml. The reaction was initiated by quickly mixing the two solutions and a portion of the mixed solution was at once transferred to a 1-cm quartz cell. The reference cell contained the same concentration of phosphate buffer solution. The cells were placed in the Cary 14 spectrophotometer and the change in absorbance of xenon trioxide at 200 mμ was recorded as a function of time. Hydrogen peroxide and *t*-butanol do not absorb at these low concentrations.

The spectrophotometric titration method was based on the fact that both hydrogen peroxide and xenon trioxide absorb at 200 mμ. For this determination 2·5 ml of a solution of $8{\cdot}15 \times 10^{-4}M$ hydrogen peroxide in 0·08*M* perchloric acid was placed in a 1-cm quartz cell. The reference cell contained the same concentration of perchloric acid. The absorbance of the peroxide was measured at 200 mμ. Then on addition of 50-μl increments of $2{\cdot}7 \times 10^{-3}M$ XeO_3 the absorbance decreased to reach a minimum near the equivalence point. Each reading was taken after allowing 30 sec for complete reaction. With excess of xenon trioxide added the absorbance increased. The intersection of two straight lines drawn through these points was the equivalence point.

For the titrimetric determination, solutions were prepared by transferring aliquots of standard hydrogen peroxide, buffer, and excess of xenon trioxide into 50-ml Erlenmeyer flasks. These solutions were diluted to 22 ml with triply distilled water. Preliminary experiments at room temperature were run to determine the minimum time for complete oxidation of hydrogen peroxide. After the reaction was complete, the solution was acidified with perchloric acid, sodium iodide was added, and the liberated tri-iodide titrated with standard thiosulphate solution. The amount of xenon trioxide consumed was equal to the difference between a blank run (no hydrogen peroxide) and the run with hydrogen peroxide. A plot of xenon trioxide consumed *vs.* hydrogen peroxide taken was made to determine the amount of hydrogen peroxide in an unknown solution. Regression analysis was used to find the intercept and slope of the resulting linear plot.

RESULTS AND DISCUSSION

Catalytic determination

Aqueous xenon trioxide will not oxidize dilute solutions of *t*-butanol. However, the reaction can be initiated by the addition of hydrogen peroxide as catalyst. The time of initiation of the reaction (τ) depends on the concentration of hydrogen peroxide as is shown in Fig. 1. This fact can be utilized for determining amounts of hydrogen peroxide as low as 0·9 μg or 36 parts per milliard. A log–log plot of hydrogen peroxide *vs.* τ or of hydrogen peroxide against the time needed to halve the initial absorbance of xenon trioxide at 200 mμ gives a straight line as shown in Fig. 2. The concentration of hydrogen peroxide can be read directly from the log–log plot, giving the results as shown in Table I. The relative precision decreased from about $\pm 3\%$ at the higher concentration to about $\pm 15\%$ at the lower concentrations.

This method is very sensitive to trace impurities in the solution. The halide ions (Cl^-, Br^-, I^-) interfere in the determination by increasing the initiation time but do not reduce the precision of the method. Metal ions such as copper(II) and

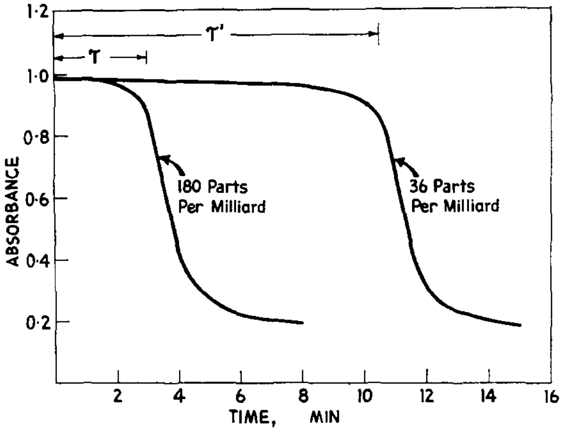

FIG. 1.—Effect of hydrogen peroxide concentration on reaction time.

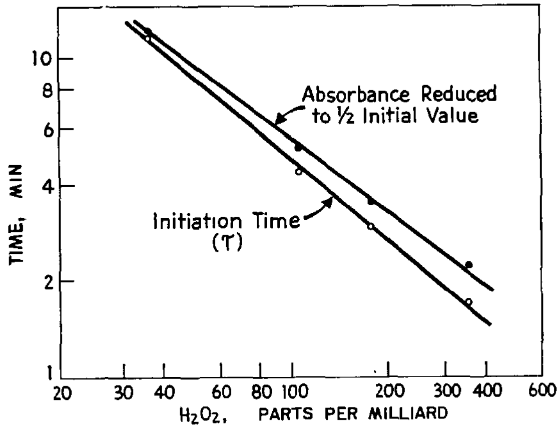

FIG. 2.—Determination of hydrogen peroxide by change in reaction time.

TABLE I.—CATALYTIC DETERMINATION OF HYDROGEN PEROXIDE

From initiation time			From half-life		
Time, *min*	Taken *ppM**	Found *ppM*	Time, *min*	Taken, *ppM*	Found, *ppM*
1·7	360	350	2·3	360	345
3·0	180	175	3·6	180	185
4·4	108	112	5·0	108	112
10·5	36	34	11·1	36	34

* *ppM* = parts per milliard = parts per(American) billion = parts per 10^9.

iron(III) increase the rate of reaction. Trace amounts of organic compounds which are easily oxidized by aqueous xenon trioxide also interfere in the determination. Phosphate, perchlorate, sulphate, fluoride and nitrate ions at low concentration have little effect on the catalytic determination. For precise results, the unknown solution should be run the same day under conditions identical to those used in obtaining values for known solutions.

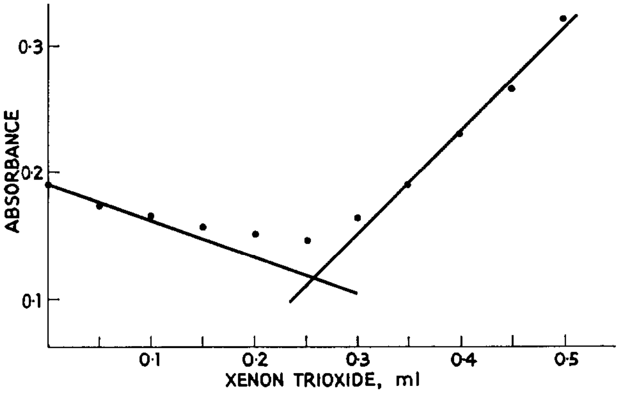

FIG. 3.—Spectrophotometric titration of hydrogen peroxide by xenon trioxide.

Spectrophotometric titration

The spectrophotometric titration was carried out by measuring the change in absorbance at 200 mμ as xenon trioxide was added to hydrogen peroxide. The results of this determination are given in Fig. 3. This method is good for determining hydrogen peroxide to a lower limit of about 50 μg or 20 ppm, as shown in Fig. 3 where 2·04 μmole of hydrogen peroxide were taken and 2·12 μmole were found; the error found was within $\pm 4\%$ which decreased to $\pm 2\%$ for amounts higher than 120 μg. Higher amounts of hydrogen peroxide give a better titration curve. Titrations run at pH higher than 1 are not as precise because the reaction is slower. Interfering ions in this determination were similar to those found in the catalytic method described above.

Titrimetric determination

The results of the titrimetric determination of hydrogen peroxide with xenon trioxide at pH 1 are summarized in Table II. Similar results were found at pH 10. The rate of the reaction is pH-dependent. At pH 10 the reaction was complete in less than 1 min, while at pH 1 the reaction required about 5 min. In general, the larger the excess of xenon trioxide, the faster the reaction.

A plot of the amount of xenon trioxide consumed against the amount of hydrogen peroxide taken gives a straight line which on extrapolation has intercept c and slope m. The values for these constants are given in the footnote to Table II. The theoretical intercept c should be zero, and the slope m should be equivalent to the stoichiometric ratio of xenon trioxide to hydrogen peroxide (1 : 3) for a complete oxidation of hydrogen peroxide to oxygen. The small observed deviations from the theoretical value may be caused by trace impurities in the water and by short-lived species of xenon in oxidation states lower than xenon(VI),[10] such as XeO_2 or XeO, which can react with water to produce small amounts of hydrogen peroxide.

The titrimetric method may be used to determine hydrogen peroxide in amounts as low as 50 μg, with relative standard deviation 4 %, which decreases to 1 % for amounts over 200 μg. Sulphate, nitrate, phosphate and fluoride ions do not interfere.

TABLE II.—TITRIMETRIC DETERMINATION OF HYDROGEN PEROXIDE BY OXIDATION WITH XENON TRIOXIDE

Xenon trioxide consumed, *μmole*	Hydrogen peroxide, *μmole* Taken	Found*
1·72	2·57	2·57
2·64	5·14	5·12
3·59	7·71	7·75
5·40	12·85	12·75
10·1	25·70	25·76
14·72	38·55	38·52

* Calculated from the equation $y = c + mx$ by least squares treatment of data where y is *μmole* of xenon trioxide consumed and x is μmole of hydrogen peroxide taken. Values for c, m, and m' (the theoretical slope for hydrogen peroxide completely oxidized to oxygen) are respectively 0·787, 0·362, and 0·333.

Easily oxidized compounds such as alcohols, aldehydes, ketones, and organic acids as well as halides (I^-, Br^-, Cl^-) interfere in the determination of hydrogen peroxide. However, this interference is dependent on the amount of contaminant present and can sometimes be overcome. As an example, the addition of chloride in an amount twelve times the concentration of hydrogen peroxide increased the time of reaction to 15 min. Higher concentration of chloride further increases the time for reaction. A plot of xenon trioxide used *vs*. hydrogen peroxide taken gave a straight line passing through the origin with a slope of 0·336 as compared to the theoretical 0·333. This appears to indicate a more stoichiometric reaction than without choride and may mean that xenon trioxide oxidized the chloride to chlorine or a higher oxidation state, which in turn oxidized hydrogen peroxide to oxygen.

It was found that acetic acid did not interfere if an equivalent amount of chloride was added or if the acid strength was increased to $3M$ perchloric acid. The total reaction time was 60 min for chloride additions and 15 min for the determinations run in $3M$ perchloric acid.

It was not possible to determine hydrogen peroxide in the presence of organic peracids, for xenon trioxide would not oxidize the peracid but the peracid interfered in the iodometric determination of excess of xenon trioxide.

A direct titration of hydrogen peroxide with xenon trioxide was attempted, with Bromocresol Purple as a redox indicator. The titration was carried out in alkaline bromide media over the pH range 8–10, with sodium carbonate or sodium borate used as a buffer. The results were erratic and not reproducible. It appeared that the indicator was destructively oxidized by xenon trioxide. A more stable redox indicator may offer a better chance for this method.

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Zusammenfassung—Wäßrige Xenontrioxidlösung wurde als Oxidationsmittel bei drei genauen Methoden zur Bestimmung von Wasserstoffperoxid verwendet. Eine katalytische Methode wird beschrieben, die Wasserstoffperoxid zur Einleitung der Reaktion zwischen *t*-Butanol und Xenontrioxid verwendet und Wasserstoffperoxid-Mengen bis 0, 9 μg oder 36 ppb zu bestimmen gestattet. Eine direkte spektrophotometrische Methode hatte eine untere Grenze von etwa 50 μg oder 20 ppm. Außerdem wurde eine indirekte titrimetrische Methode verwendet, um Wasserstoffperoxid in Mengen von 50 μg mit einer relativen Standardabweichung von 4% zu bestimmen, die bei Mengen über 200 μg auf 1% abnimmt.

Résumé—On a utilisé une solution aqueuse de trioxyde xénon comme agent oxydant dans trois méthodes précises d'analyse de l'eau oxygénée. On décrit une méthode catalytique, qui utilise l'eau oxygénée pour amorcer la réaction entre le *t*-butanol et le trioxyde de xénon, pour déterminer des quantités d'eau oxygénée aussi petes que 0,9 μg ou 36 parties par milliard (ppM). On a trouvé qu'un titrage spectrophotométrique direct a une limite inférieure de 50 μg ou p.p.m. On a aussi utilisé une méthode titrimétrique indirecte pour doser l'eau oxygénée en quantités aussi faibles que 50 μg avec un écart type relatif de 4%, qui s'abaisse à 1% pour des quantités supérieures à 200 μg.

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APPLICATIONS OF ENZYME-CATALYSED REACTIONS IN TRACE ANALYSIS—I

DETERMINATION OF MERCURY AND SILVER BY THEIR INHIBITION OF INVERTASE

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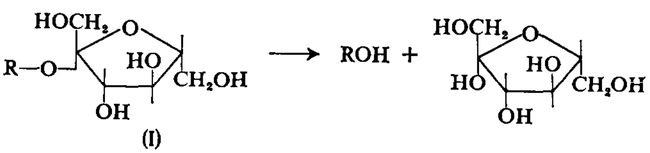
Summary—Procedures are described for the accurate determination of silver (2–10 × $10^{-7}M$) and mercury(II) (2–10 × $10^{-8}M$) in the presence of each other and of most other metals. The methods are based on the inhibition by these metals of invertase catalysis of the hydrolysis of sucrose.

ENZYMES are very efficient catalysts; their catalytic effect can be detected when they are present in $<10^{-8}M$ concentrations. Moreover, these macromolecules are often influenced by equally small concentrations of metal ions, anions and organic molecules. These effects have been used for the determination of specific inhibitors for enzymes, such as pesticides,[1] but there are only a few recorded applications to the analysis of trace metals or simple anions. The inhibition of liver esterase by fluoride has been used to determine >0·004 ppm of fluoride,[2] and the inhibition of xanthine oxidase by silver and mercury[3] has been applied to their determination in solutions >2·5 × $10^{-7}M$. Finally, the activation of isocitric dehydrogenase has been used for the determination of manganese, zinc, magnesium and cobalt[4] at concentrations 10^{-6}–$10^{-8}M$.

This paper describes an investigation of the effect of metal ions on the catalysis of the hydrolysis (inversion) of sucrose by invertase (β-fructofuranosidease). On the basis of the results obtained, sensitive and selective methods for the determination of silver and mercury have been devised. The methods are simple and relatively rapid and could be adapted for automated analysis.

The enzyme

Yeast invertase is one of the most readily available and least expensive enzymes. It has never been obtained in a homogeneous or crystalline form (because yeast gum, a polymannan, accompanies the enzyme through most purification procedures[5]) and is supplied as a concentrate. It catalyses the hydrolysis only of β-fructofuranosides (I), of which sucrose (I, R = 1-α-glucopyranosyl)


(I)

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is the commonest example and is the substrate used in the present studies. This reaction can be followed in a number of ways, but one of the simplest is to measure the change in optical rotation during the hydrolysis reaction. This has been used in the present investigation.

Much information is available about the inhibition of invertase. Mercury(I) and mercury(II) inhibit strongly at pH 4–7, and the inhibition is reversible but slow.[6,7] Silver is also a strong inhibitor; copper(II), cadmium, zinc and uranium(VI) inhibit less strongly, but in each instance the inhibition is reversible and instantaneous.[6,8] Other inhibitors are organomercury compounds,[7] aromatic amines,[6] anionic surfactants[9] (at pH < 4) and iodine.[10] From these previous investigations, it seemed likely that methods for the determination of mercury(II) at the $10^{-7}M$ level and silver at rather higher concentrations could be devised on the basis of their inhibition of invertase.

Behaviour of invertase in the absence of inhibitors

Before evaluating the effect of inhibitors on the enzyme, it was necessary to investigate the behaviour of the enzyme in the absence of metal ions. In all instances, the efficiency of the enzyme was appraised by measuring the amount of hydrolysis of a given amount of sucrose in a given time (usually 30 min). The effect of pH on the enzyme activity is shown in Fig. 1 (curve *a*). The maximum efficiency (Relative Activity = 1·00) occurred at pH 4·5 as found previously,[6] but there is little change in efficiency between pH 4·0 and pH 5·5. The decrease in efficiency at pH $>$ 5·5 has the form of a dissociation curve, and has been explained by assuming that the enzyme becomes inactive when certain weakly acidic groups ($pK_A \sim 7$) dissociate.[11] However, this part of the curve is independent of the substrate, which indicates that these groups are not involved in substrate binding.[12] Certain basic groups ($pK_B \sim 3$) are thought to bind the substrate.[6] The rate of sucrose hydrolysis was found to be directly proportional to the enzyme concentration.

Inhibition by silver ions

The inhibiting effect of different amounts of silver ions at various pH values is shown in Fig. 1. Maximal inhibition relative to the activity of the free enzyme occurs at pH 5·5. Fig. 2 shows the variation of inhibition with silver concentration for various amounts of enzyme, at pH 5·5. The middle curve shows that the reaction of silver with the enzyme is instantaneous, because incubation of silver with the enzyme did not enhance the inhibition, and that it is non-competitive, *i.e.*, the silver and the substrate bind at different sites on the enzyme. The absence of inhibition by $<$ *ca.* $10^{-6}M$ silver is due, apparently, to the binding of silver by impurities in the enzyme solutions.[7] This is borne out by the fact that the amounts of silver required to overcome this region of non-inhibition increase with increasing amount of enzyme solution added, as is shown in Fig. 2. After this region, the curves are parallel, which indicates that the amount of silver bound by the enzyme is small compared with the amount of free silver ions present.

As the rate of sucrose hydrolysis is directly proportional to the enzyme concentration, the relative concentrations of enzyme in various solutions are given by the ratio of the hydrolysis rates in these solutions. This can also be used to estimate the relative

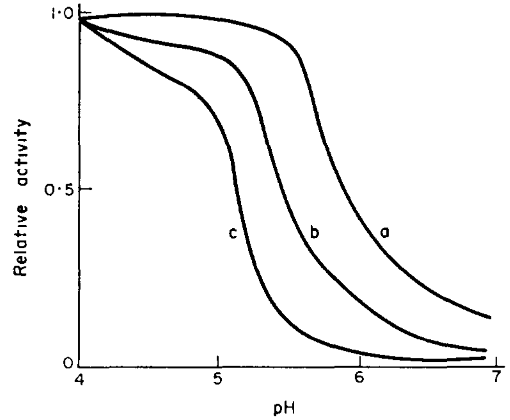

FIG. 1.—Change in invertase activity with pH.
(*a*) free enzyme; (*b*) enzyme + 2 × $10^{-6}M$ Ag$^+$; (*c*) enzyme + 5 × $10^{-6}M$ Ag$^+$.
R.A. at pH 4·48 = 1·00.

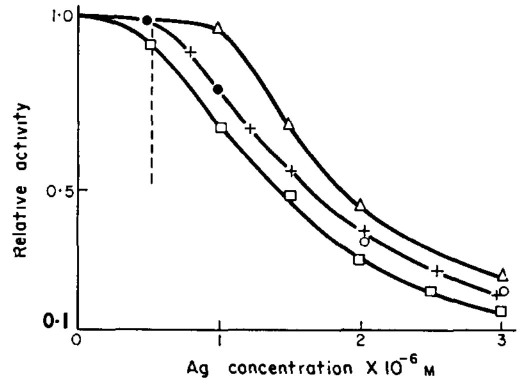

FIG. 2.—Invertase activity at pH 5·5 as a function of Ag$^+$ concentration.
Enzyme used (ml): □ 0·5; ○ 1·0 (incubated); × 1·0 (non-incubated); △ 2·0.
Dotted line indicates Ag$^+$ concentration bound by impurities in 1 ml of enzyme solution.

concentrations of free enzyme in solutions containing silver ions, and it can readily be shown that

$$[\mathrm{E}](1\text{-}R.A.) = [\mathrm{Ag}_n\mathrm{E}]R.A. \tag{1}$$

where [E] is the concentration of free enzyme, [Ag$_n$E] is the concentration of inhibited enzyme, n is the number of silver ions bound per site on the enzyme molecule and *R.A.* is the activity (reaction rate) relative to that of the uninhibited enzyme at the same pH. Likewise, the stability constant of the silver–enzyme site complex ($K_{n\mathrm{Ag}}$) is given[13] by

$$K_{n\mathrm{Ag}} = \frac{[\mathrm{E}][\mathrm{Ag}]^n}{[\mathrm{Ag}_n\mathrm{E}]} \tag{2}$$

Combination of equations (1) and (2) gives

$$\frac{(1\text{-}R.A.)}{R.A.} = \frac{[\mathrm{Ag}]^n}{K_{n\mathrm{Ag}}} \tag{3}$$

When $[Ag_nE] \ll [Ag]$, as in the present example, [Ag] in equation (3) can be replaced by $[Ag]_t$, the total concentration of silver ions added. Thus a plot of log (1-*R.A.*)/*R.A.* against log $[Ag]_t$ should give a straight line of slope *n* and intercept (log K_{nAg})/*n* on the log [Ag] axis. In the present study, allowance was made for silver bound by impurities so that $[Ag]_t$ was the total concentration of silver added minus that bound by impurities. Such a plot is shown in Fig. 3, from the results in Fig. 2. The slope is 1·97, showing that two silver ions are bound per site, as found by Myrbäck,[13] and the value of K_{2Ag} calculated from the intercept value of 5·93 is 2×10^{-12} mole^2.l.$^{-2}$, as compared with $1{\cdot}32 \times 10^{-12}$ mole^2.l.$^{-2}$ found at pH 5·3 and 1×10^{-12} at pH 5·6 by Myrbäck[13] using a purer enzyme preparation, at 30°. It should be emphasized that these are equilibrium constants for the proton displacement reaction:[13]

$$2Ag^+ + HE \rightleftharpoons H^+ + Ag_2E^+.$$

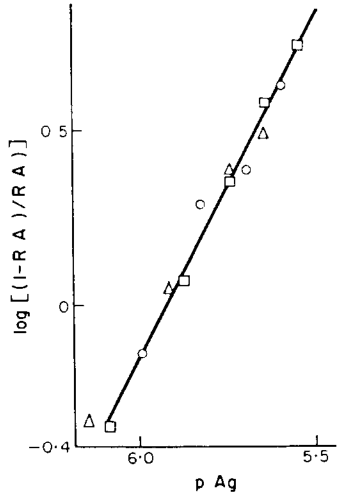

FIG. 3.—Determination of stability of enzyme–silver complex from results in Fig. 2.

Determination of silver

Figure 2 shows that the enzyme (1 ml) responds most sensitively at pH 5·5 to silver concentrations in the range 1–2 × $10^{-6}M$. Furthermore, if a known amount of silver ($1{\cdot}00 \times 10^{-6}M$) is added to all solutions sufficient to complex with all silver-binding impurities present, the most sensitive range is then 0–10 × $10^{-7}M$ silver. An almost linear calibration curve is obtained by using this procedure. Results for the analysis of pure silver nitrate solutions by this method are summarized in Table I.

Inhibition by mercury(II) ions

The variation in inhibition by different amounts of mercury(II) acetate with pH is given in Fig. 4. These curves have a different shape from those for silver inhibition. In particular, mercury inhibits strongly at pH 4, and the enzyme is about a hundred times more sensitive to mercury than it is to silver. Incubating mercury with the enzyme (Fig. 5) showed, as expected,[6,7] that greater inhibition occurred after incubation for 30 min before starting the hydrolysis. From these results it was also possible

TABLE I.—ANALYSIS OF PURE SILVER NITRATE SOLUTIONS

Ag added, $10^{-7}M$	Ag found, $10^{-7}M$	
2·0	2·1, 2·2	
3·0	2·8, 3·1, 2·8	Mean error
5·0	4·9, 4·8, 5·0	$\pm 1{\cdot}2 \times 10^{-8}M$
6·0	6·1, 6·2, 6·1	
8·0	8·0, 8·0	

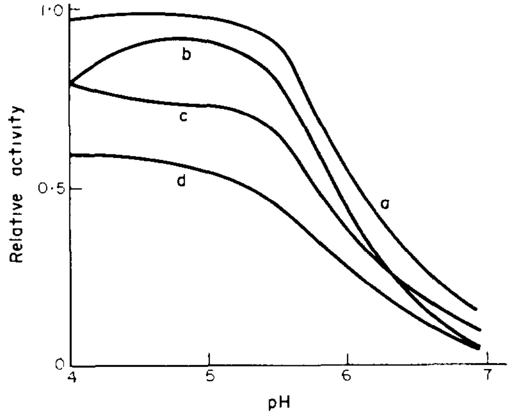

FIG. 4.—Change in invertase activity with pH.
(*a*) free enzyme; (*b*) enzyme $+1{\cdot}2 \times 10^{-6}M$ $AuCl_4^-$; (*c*) enzyme $+10^{-7}M$ Hg(II); (*d*) enzyme $+ 2 \times 10^{-7}M$ Hg(II).

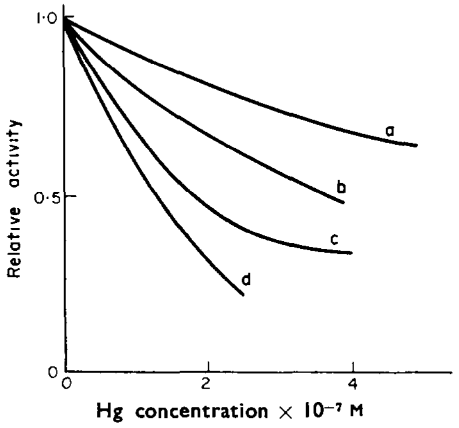

FIG. 5.—Invertase activity at pH 5·5 as a function of Hg concentration.
(*a*) Hg(I), not incubated; (*b*) Hg(II), not incubated; (*c*) Hg(I), incubated; (*d*) Hg(II), incubated.

to calculate that inhibition was competitive. Because the amount of mercury bound by the enzyme is not small compared with the amount of mercury added, the number of mercury ions bound per enzyme site and the stability constant of the complex could not be calculated, as was done for silver.

In the presence of $10^{-7}M$ mercury(II), a small increase in inhibition was caused by $<2 \times 10^{-7}M$ silver. As such a small amount of silver does not usually inhibit the enzyme, the silver must be complexing with impurities that compete with mercury for enzyme sites.

Determination of mercury(II)

If the inhibition curve is reproducible, it should be possible to determine $0–10 \times 10^{-8}M$ mercury(II) by its inhibitory effect, after incubation with the enzyme. Experiments showed that reproducible calibration curves could be obtained. Results for the analysis of pure mercury(II) chloride solutions by this method are summarized in Table II. The results are less precise than those for silver, but it must be remembered that the concentrations of mercury involved are an order of magnitude less than those of silver. Better precision is obtained if the calibration graph is obtained from solutions of concentrations similar to the unknowns.

TABLE II.—ANALYSIS OF PURE MERCURY (II) CHLORIDE SOLUTIONS

Hg taken $10^{-8}M$	1·9	2·5	3·4	3·4	4·0	5·6	5·6	6·4	6·4	8·5	8·5	
Hg found* $10^{-8}M$	2·4	2·8	3·5	3·4	4·1	5·8	5·3	6·7	6·1	8·6	8·6	
Hg taken $10^{-8}M$	5·0	5·0	5·0				5·0					
Hg found* $10^{-8}M$	4·75	4·6	5·1	†5·2	4·75	5·15	5·2	4·9	5·1	5·3	5·05	5·2
		(mean 4·8)				(mean 5·1, coeff. of variation 4%)						

* Using a calibration curve of $1–10 \times 10^{-8}M$ mercury(II)
† Using a calibration curve of $4–6 \times 10^{-8}M$ mercury(II).

Effects of other cations

Although mercury and silver are the most likely metals to be amenable to determination in this way, a representative sample of other metal ions was also investigated for inhibitory or other effects on invertase. Mercury(I) is similar to, but less effective than mercury(II), as shown in Fig. 5. Incubation increased the inhibition. The effect of other cations is given in Table III. Only copper and gold gave sensitive inhibition effects. Inhibition by $10^{-5}M$ copper was significant, but was not considered sensitive enough for the development of an analytical method. Gold was even more sensitive. The dependence of gold inhibition on pH is included in Fig. 4. Again the most sensitive inhibitory effect was at pH 5·5 although little change occurred between pH 5·5 and 6·0. Figure 6 shows the inhibition by various amounts of gold in both incubated and non-incubated systems. The inhibition becomes erratic at gold concentrations, above $3–4 \times 10^{-6}M$ and for this reason attempts to develop a method for gold were not continued.

The effect of anions and thiourea

Species that complex with silver or mercury will compete with the enzyme for these metals, and, if present in sufficient amounts, will counteract the inhibitory effects.

TABLE III.—EFFECT OF OTHER METAL IONS ON INVERTASE AT pH 5·5

Ion	—	Au(III)	Cd		Ce(IV)	Co(II)	Cu(II)	Gd(III)	In(III)
Conc., *ppm*	—	2·4	100	0·1	70	100	6·4	8	40
R.A.	1·00	0·60	0·51	1·00	0·61	0·70	0·25	0·95	0·80

Ion	Mn(II)	Mo(VI)	Ni	Pb	Pd(II)	Sr	UO_2(II)	Zn		Zr(IV)
Conc., *ppm*	100	4	100	100	100	500	100	100	0·06	100
R.A.	0·93	0·99	0·75	0·47	0·70	0·96	0·41	0·32	1·00	0·98

Bi(III), Cr(III), Fe(II), Sn(II) (all 100 ppm), Ta(IV) (20 ppm), Tl(I) (200 ppm) and V(IV) (50 ppm) all gave *R.A.* 1·00.

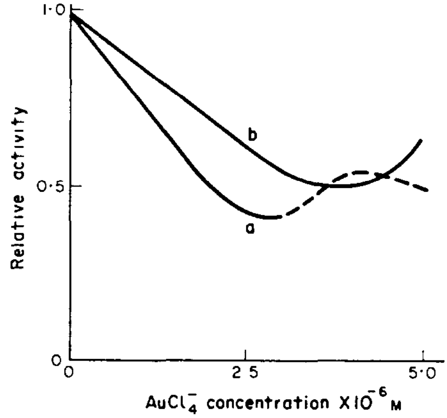

FIG. 6.—Invertase activity at pH 5·5 as a function of $AuCl_4^-$ concentration.
(*a*) incubated; (*b*) non-incubated.

The effects of all the common anions on the inhibition by these metals was therefore, investigated and the maximal concentration of each that could be tolerated in the determination of silver and mercury was found. These results are summarized in Table IV. None of these species had any effect on the activity of the free enzyme.

TABLE IV.—MAXIMAL ANION CONCENTRATIONS (*M*) TOLERABLE IN THE DETERMINATIONS OF MERCURY(II) AND SILVER

Anion	Cl^-	Br^-	I^-	F^-	CN^-	S^{2-}	NO_3^-
Ag*	5×10^{-5}	$<10^{-5}$	$<10^{-6}$	2×10^{-3}‡	10^{-7}	2×10^{-7}	2×10^{-3}‡
Hg†	2×10^{-5}	2×10^{-5}	$<10^{-7}$	$<10^{-5}$	$<10^{-8}$	3×10^{-9}	2×10^{-3}‡

Anion	SO_4^{2-}	NO_2^-	SCN^-	CO_3^{2-}	PO_4^{3-}	thiourea	Teepol
Ag*	2×10^{-5}	2×10^{-3}‡	2×10^{-6}	2×10^{-3}‡	2×10^{-3}‡	$<10^{-8}$	1%‡
Hg†	2×10^{-4}	2×10^{-3}‡	2×10^{-5}	2×10^{-3}‡	2×10^{-5}	$<10^{-5}$	1%‡

* Total Ag concentration $6 \times 10^{-6}M$.
† Hg concentration $1{\cdot}25 \times 10^{-7}M$.
‡ The effect of larger concentrations was not investigated.

As expected, only small amounts of cyanide, sulphide, iodide, bromide, thiocyanate and thiourea could be tolerated. In fact, it is possible to use this re-activation of the inhibited enzyme for the determination of traces of these anions. This will be reported in Part II.[14] Thiourea had a unique effect. It enhanced the inhibition by silver when present in similar concentrations to that of silver.

Determination of silver in the presence of mercury(II) and other metals

Mercury(II) is the most sensitive inhibitor of invertase, and thus even very small concentrations will interfere in the determination of silver. Interference from $< 10^{-7}M$ mercury(II) can be avoided by not incubating the enzyme with the test solution, because mercury is competitively and only slowly bound by the enzyme, whereas silver binding is instantaneous and non-competitive. For greater concentrations of mercury, however, it was necessary to use a masking agent as well as not incubating the enzyme and the metal ions. EDTA-type ligands complex mercury much more strongly than silver. The relative activity of the enzyme in the presence of these metal ions and various amounts of EDTA, nitrilotriacetic acid (NTA) and 1,2-diaminopropane-*N*,*N*,*N*′,*N*-tetra-acetic acid (DPTA) are given in Table V. DPTA ($10^{-3}M$) completely overcame mercury inhibition whilst affecting that by silver least and experiments were carried out to determine silver in the presence of mercury, using $10^{-3}M$ DPTA. The results are included in Table VI. The results are all slightly high, and not more than a five-fold excess of mercury can be tolerated.

TABLE V.—EFFECT OF CHELATING AGENTS ON INHIBITION BY MERCURY(II) AND SILVER

Ligand	—	EDTA	EDTA	—	NTA	DPTA
Concentration	—	$10^{-5}M$	$10^{-4}M$	—	$10^{-3}M$	$10^{-3}M$
R.A. with silver*	0·58	0·60	0·84	0·67	0·84	0·79
R.A. with mercury*	0·44	0·73	1·00	0·42	0·99	1·00

* $2 \times 10^{-6}M$.

TABLE VI.—DETERMINATION OF SILVER IN THE PRESENCE OF OTHER METAL IONS

Cation added	Concentration, M	Ag taken, $10^{-7}M$	Ag found, $10^{-7}M$
Hg(II)	10^{-6}	3·0	3·2, 3·2, 3·1
	10^{-6}	5·0	5·3, 5·1, 5·2
	10^{-6}	4·0	4·1, 4·1
	2×10^{-6}	4·0	4·3, 4·2
	3×10^{-6}	4·0	4·9, 5·0
UO_2(II)	4×10^{-5}	2·0	2·0, 2·2
		5·0	5·4, 5·1
		8·0	8·0, 8·1
Zn	10^{-4}	3·0	3·1, 3·0
		5·0	4·9, 5·0
		7·0	$7{\cdot}0_5$ $7{\cdot}0_5$
Pb	5×10^{-5}	3·0	3·2, 2·9
		5·0	5·1, 4·8
		7·0	6·9, 7·1
Cd	10^{-4}	3·0	3·2, 3·1
		5·0	5·2, 5·1
		7·0	$7{\cdot}0_5$, $7{\cdot}0_5$
Cu(II)	10^{-4}	3·0	3·0, 2·9
		5·0	4·9, 4·9
		7·0	7·1, 6·9

The other metal ions that inhibit the enzyme do so immediately, so that non-incubation would not reduce their effect. However, $10^{-3}M$ DPTA should be able to mask all the interfering ions in Table III except for $AuCl_4^-$. Results for the determination of silver in the presence of DPTA and other metal ions are given in Table VI. They confirm that silver can be determined accurately and precisely in the presence of at least 100-fold excesses of copper(II), cadmium, lead, uranium(VI) and zinc, when $10^{-3}M$ DPTA is present. DPTA did not prevent interference by $AuCl_4^-$.

Determination of mercury(II) in the presence of other cations

There are no readily accessible ligands that bind silver much more strongly than mercury, so that it will not be possible to mask the effect of silver. However, if the enzyme-catalysed hydrolysis is carried out at pH 4·0, the inhibitory effect of silver is virtually eliminated, whereas that of mercury is only slightly decreased (*cf.* Figs. 1 and 4). Even this slight decrease could be reduced by incubating the enzyme with the metal ions at pH 5·5, and carrying out the hydrolysis at pH 4·0. On changing the pH, the inhibitory effect of the other metal ions will instantaneously disappear, whereas that of mercury would only slowly decrease to the lesser inhibition at pH 4·0. Such a procedure gave a sensitivity for mercury very similar to that in Table II. A comparison of the effect of other ions on the final optical rotation of the solution inhibited by $1{\cdot}00 \times 10^{-7}M$ mercury(II) is given in Table VII. It shows that this concentration of mercury can be determined in the presence of cadmium ($5 \times 10^{-3}M$), zinc ($1{\cdot}5 \times 10^{-3}M$), lead ($5 \times 10^{-4}M$), uranium ($4 \times 10^{-4}M$) and copper ($10^{-5}M$), and with exceptional accuracy in the presence of small amounts of silver ($3 \times 10^{-6}M$).

TABLE VII.—EFFECT OF OTHER IONS ON THE DETERMINATION OF $10^{-7}M$ MERCURY(II)

Ion added	—	Ag	Ag	Ag	—	Zn	Pb	Cd
Conc.,	—	10^{-6}	2×10^{-6}	3×10^{-6}	—	$1{\cdot}5 \times 10^{-3}$	5×10^{-4}	9×19^{-4}
Optical rotation	2·41	2·42*	2·40*	2·44*	2·22	2·19	2·46	1·72†

Ion added	—	Cu(II)	Pb	UO_2(II)	—	Cd‡	Cd‡	Pb	UO_2(II)
Conc., *M*	—	10^{-5}	5×10^{-4}	4×10^{-4}	—	5×10^{-3}	5×10^{-5}	5×10^{-5}	4×10^{-5}
Optical rotation	2·07	2·05	2·23	2·31	1·98	1·95	1·96	1·96	1·97

* ≡10·03, 9·98, $10{\cdot}05.10^{-8}M$ respectively.

† Precipitate formed on quenching reaction with Na_2CO_3; sucrose co-precipitated.

‡ EDTA added to prevent precipitation with Na_2CO_3.

Enzyme stability

Analytical chemists, especially those concerned with inorganic analysis, have have never favoured the use of enzymes in analytical methods. This is probably a result of an in-bred feeling that the stability and purity of enzymes, and the reproducibility of their catalytic effect, are inferior to those of simpler chemicals, and that enzyme-catalysed reactions are too slow, and too sensitive to other chemicals that might be present, to be of any use in everyday inorganic analysis. The present investigation and the work of earlier investigators,[2–4] however, have shown that the results obtained by enzymatic inhibition or enhancement are as precise as any other method of analysis at these low concentrations. This investigation has also shown that a host of foreign ions can be tolerated, and that the longest determination need take little longer than an hour. Enzymes are now much more readily available and much purer than they were a few years ago, and even if the enzyme is not completely pure, the impurities need not be detrimental to its performance. Thus, only the stability of the enzyme needs to be established.

The invertase used in this investigation was prepared by the dilution of a concentrate. This dilute solution (in pH 5·5 buffer) lost $< 5\%$ of its activity over 6 days at room temperature, although the solution became cloudy after 3–4 days. During the same time, a similar decrease in the sensitivity of the enzyme to silver was observed, but there was no change in its sensitivity to mercury(II).

The enzyme concentrate was stored in a stoppered bottle at 2°. When a newly purchased bottle was first opened, the enzyme was twice as active as the "normal" value claimed by the manufacturers, and was inhibited by very small ($4–20 \times 10^{-8}M$) concentrations of silver at pH 4·0. This inhibition, however, only reduced the enzyme activity to its "normal" value. Thus this additional activity is not due to invertase. After a week, activity of the enzyme had become "normal"; an unopened bottle stored at 2° for 7 months also only had normal activity. Apart from this abnormal effect, two long-term deterioration effects were observed for the concentrate. First, there was a gradual increase in the concentration of silver binding impurities, so that the enzyme became increasingly less sensitive to silver. However, the slope of the inhibition curve was unchanged. Thus a suitable increase in the amount of silver added to overcome the effect of these impurities is sufficient to counteract this. Secondly, as the concentrate aged, the dilute solution prepared from it clouded more rapidly. Solutions prepared from a 7-month old concentrate remained clear only for a day. As these long terms changes did not occur in an unopened bottle of concentrate, it must be assumed that they are due to aerial oxidation or to attack by aerial organisms. Thus an opened bottle stored at 2° may be used for six months. Presumably an unopened bottle will keep for years at 2°.

Adsorption of mercury and silver by glassware

A difficulty associated with all methods of determining such low concentrations of metal ions in solution is the adsorption of these ions on the glass apparatus used. Silver is particularly prone to adsorption on glass,[15,16] and this has recently been studied in detail.[17] In the present work, no measurable adsorption of silver was observed in the time required for the analyses, but as a precaution all solutions were prepared by diluting a $10^{-4}M$ stock solution of silver immediately before use.

Mercury was adsorbed onto the glassware in amounts that were appreciable when related to the determination of $1–10 \times 10^{-8}M$ mercury. No adsorption was found to occur in the first 4 hr of contact but adsorption increased markedly after that time. Dilute mercury solutions were therefore prepared from a much more concentrated solution immediately before use.

EXPERIMENTAL

Chemicals

Invertase concentrate (Hopkin and Williams)
DPTA (Hopkin and Williams)

All other chemicals were analytical reagent grade or of high purity, except for the acetic acid, sodium hydroxide and sodium carbonate, which were general purpose reagent grade.

Solutions

Invertase. Concentrate (1 ml) and pH 5·5 buffer (5 ml) were diluted to 100 ml. The solution was discarded when it became cloudy.

Buffer (pH 4·0 or 5·5). Acetic acid neutralized with sodium hydroxide solution to the required pH, so that the final total acetate concentration was $5M$.

Sucrose. A 50% aqueous solution.

Buffered sucrose. Sucrose (50 g) and pH 5·5 or 4·0 buffer solution (50 ml) made up to 100 ml.

DPTA. A $10^{-2}M$ aqueous solution.

Stock silver nitrate solution, $10^{-4}M$. More dilute solutions were obtained by appropriate dilution immediately before use.

Stock mercury solution, $10^{-4}M$. The acetate or chloride was used. More dilute solutions were obtained by appropriate dilution immediately before use.

Sodium carbonate solution, $1M$.

Anion and cation interferences were investigated with common salts of the species.

Procedures

The hydrolysis was followed by measuring the optical rotation, $[\alpha]_D$, after 30·0 or 60·0 min at 30°, in a 10-cm polarimeter cell. The change in optical rotation was proportional to time over the first 60 min of the hydrolysis. The reaction was quenched after 30 or 60 min by adding sodium carbonate so that optical rotation measurements could be made some time later if desired. In the determinations of mercury and silver, it is sufficient to measure the final optical rotation and to prepare calibration graphs from these measurements. In the investigations that led to the establishment of these procedures, however, it was more meaningful to measure the relative activity (*R.A.*) of the enzyme in different circumstances. This was measured by determining the *change* in optical rotation $\Delta\,[\alpha]_D$ during the reaction and employing the relationship

$$R.A. = \frac{\Delta[\alpha]_{D(\text{given conditions})}}{\Delta[\alpha]_{D(\text{most active conditions})}}$$

Investigations at various pH values were made with acetate buffers. The pH values recorded are those of the reaction solutions.

Cation effects were measured as follows: metal ion solution (1 ml), sucrose solution (2 ml) and pH 5·5 buffer (1 ml) were mixed in a 10-ml standard flask and diluted to 9 ml, and the flask was suspended in a thermostatically-controlled water-bath at 30° for 30 min. Enzyme solution (1 ml) was added, and the optical rotation measured after 60 min. Anion effects were measured as follows: anion solution (1 ml), pH 5·5 buffer (1 ml), enzyme (1 ml) and $10^{-4}M$ silver nitrate or $10^{-6}M$ mercury (II) chloride solution (0·5 ml) were mixed in a 10-ml standard flask and diluted to 8 ml, then incubated at 30° for 30 min, Sucrose solution (2 ml) was added and the procedure was then the same as for the cations.

Determination of silver in pure solutions

In a 10-ml standard flask mix $10^{-5}M$ silver nitrate (1·00 ml)*, sample solution (5 ml), enzyme solution (1 ml) and water (0·5 ml). Suspend in a water-bath at 30° ± 0·05°. After 30 min add pH 5·5 buffered sucrose solution (2 ml) and dilute to the mark. Start a stop-clock. After a further 30·0 min, remove 5·00 ml of the solution and add it to 5·00 ml of sodium carbonate solution. Measure the optical rotation of this solution when convenient. Prepare a calibration graph ($[\alpha]_D$ *vs.* concentration) similarly.

Determination of silver in the presence of interfering cations

In a 10-ml standard flask mix together $10^{-5}M$ silver nitrate solution (1 ml), sample solution (4 ml), DPTA solution (1 ml), pH 5·5 buffered sucrose solution (2 ml) and water (1 ml). Keep at 30° for 30 min, add enzyme (1 ml), and continue as above. Prepare a calibration curve similarly.

Determination of mercury(II) in pure solution

In a 10-ml standard flask mix together sample solution (5 ml), enzyme (1 ml) and pH 5·5 buffer (1 ml) and dilute to exactly 8 ml (use flasks previously graduated at 8 ml). Keep at 30°. After 30 min add sucrose solution (2 ml), quench after 60·0 min and measure the optical rotation in the usual way. Prepare a calibration graph similarly.

* To inactivate the silver-binding impurities. The amount needed should be checked from time to time by preparing a curve as in Fig. 2.

Determination of mercury in the presence of interfering cations

Repeat the procedure above, but omit the initial addition of buffer solution. Start the reaction by adding pH 4·0 buffered sucrose solution (2 ml), then continue as above. Prepare a calibration curve by the same procedure.

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Zusammenfassung—Zur genauen Bestimmung von Silber (2–10 × $10^{-7}M$) und Quecksilber(II) (2–10 . $10^{-8}M$) nebeneinander und in Gegenwart der meisten anderen Metalle werden Arbeitsvorschriften angegeben. Die Methoden beruhen darauf, daß die Katalyse der Sucrosehydrolyse durch Invertase von diesen Metallen inhibiert wird.

Résumé—On décrit des techniques pour le dosage précis de l'argent (2–10 × $10^{-7}M$) et du mercure(II) (2–10 × $10^{-8}M$) en présence l'un de l'autre et de la plupart des autres métaux. Les méthodes sont basées sur l'inhibittion par ces métaux de la catalyse par l'invertase de l'hydrolyse du saccharose.

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LE DOSAGE DU PLOMB DANS LES EAUX ALIMENTAIRES PAR TROIS METHODES POLAROGRAPHIQUES

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Résumé—Il est important de pouvoir doser rapidement et avec une précision suffisante le plomb dans les eaux alimentaires. Les auteurs comparent les possibilités de trois méthodes polarographiques récentes: la polarographie à goutte pendante, la polarographie oscillographique différentielle à tension imposée et la polarographie à impulsion. Ils concluent a la supériorité de la polarographie à impulsion.

EN 1962, l'Organisation Mondiale de la Santé (O.M.S.) a abaissé de 100 μg/l. à 50 μg/l. la teneur maximum admissible du plomb dans les eaux alimentaires. La limite autorisée dans la plupart des pays est cependant de 100 μg/l., avec une tolérance de 300 μg/l., dans certains cas.[1,2] Outre les méthodes colorimétriques à la dithizone ou au sulfure de sodium, l'O.M.S. recommande pour le dosage du plomb la méthode polarographique. La solution idéale consiste naturellement à utiliser un appareil qui permette le dosage direct du plomb, sans séparation préalable. Le but du présent travail consiste à comparer trois méthodes polarographiques différentes, à savoir respectivement: la polarographie oscillographique différentielle à tension imposée; la polarographie à impulsion; la méthode de la goutte pendante.

La polarographie classique n'a pas été envisagée. La sensibilité de cette méthode est trop faible pour qu'il soit possible de doser directement le plomb dans les eaux de consommation. En effet, la limite de sensibilité de la méthode se situe à $5 . 10^{-6}M$, ce qui correspond à des teneurs en plomb voisines de 1 mg/l. Une eau dont la teneur en plomb se situe dans les limites admises (de 0,05 à 0,3 mg/l.) ne peut donc être analysée directement par la technique polarographique classique.

Pour que le dosage devienne possible, il convient que le plomb soit extrait de l'eau par la dithizone.[3-7] Le volume d'eau mis en oeuvre dans les méthodes reprises en références est imposant: il varie entre 500 ml et 15 l.

Nous allons montrer que les trois méthodes polarographiques que nous avons utilisées permettent de réaliser le dosage du plomb d'une manière simple et moins fatigante.

PARTIE EXPERIMENTALE

Conditions opératoires générales

L'entraînement du plomb par la décomposition progressive du bicarbonate de calcium en carbonate est empêché par addition, au moment du prélèvement, de 5 ml d'acide nitrique à 65% par litre d'eau.[8] Si l'eau n'est pas acidifiée, on constate que pour certains types d'eau, la teneur en plomb diminue avec le temps.

Les cellules polarographiques sont maintenues à la température de 25°. L'appareillage utilisé est le suivant. En polarographie à la goutte pendante, les mesures ont été effectuées au moyen d'un Polarecord E.261 Metrohm (Herisau, Suisse). Le montage de l'électrode à goutte de mercure stationnaire a été réalisé dans le laboratoire du Professeur Duyckaerts. Signalons en passant qu'il existe plusieurs versions commerciales de ce type d'électrode (Metrohm, Radiometer). En polarographie à impulsion, les polarogrammes ont été enregistrés au moyen d'un Southern-Harwell Mark II, pulse polarograph, type A.1700. En polarographie oscillographique différentielle à tension imposée, les pics ont étés observés sur l'écran d'un Davis Differential Cathode Ray Polarograph A. 1660 (Camberley, Surrey, Angleterre).

Quatre échantillons, numérotés de I à IV, d'eaux de provenances diverses ont été étudiés. Leurs caractéristiques sont reproduites dans le tableau I.

TABLEAU I

Technique utilisée	Pb, $\mu g/l$.			
	I	II	III	IV
Oscillopolarographie différentielle				
Dosage direct	1470	128		
Dosage après extraction	1430	164	11·6	12·4
Polarographie à impulsion				
Condition (*a*)	1540			
(*b*)	1570			
(*c*)		195	13·7	13·7
Goutte pendante de Hg	1290	171	2·0	2·2

Lieus de prélèvement: I—Verviers (eau de ville), pH 4,9
II—Gembloux (Faculté des Sciences agronomiques), pH 6,7
III—Liege (eau de ville), pH 7,15
IV—Barrage de la Gileppe, pH 4,9.

Oscillopolarographie différentielle à tension imposée

Par suite de certaines divergences constatées entre cette méthode et les deux autres, nous avons utilisé le dosage direct et le dosage après extraction à la dithizone. Les possibilités d'application de cette méthode ont d'ailleurs déjà fait l'objet d'une publication précédente.[9]

Dosage direct. A un volume de l'échantillon à étudier on ajoute un volume du milieu de base suivant: acétate ammonique 0,5M-acide tartrique 0,1M. Cette solution est placée dans la cellule de gauche. La cellule de droite contient le milieu de base seul dilué 2 fois. Après dégazage des deux solutions, le potentiel de départ est fixé à −0,40 V. Le pic du plomb culmine à −0,65 V, au milieu de l'écran de l'oscilloscope. La valeur de la concentration en plomb est calculée au moyen d'une courbe d'étalonnage ou par comparaison avec une solution de concentration en plomb connue et voisine de la solution à étudier.

Dosage après extraction à la dithizone. A 100 ml d'eau à analyser placés dans une ampoule à décanter de 250 ml on ajoute 5 ml de citrate ammonique 1M, et quelques gouttes de solution alcoolique de phénolphtaléine à 1%. On ajoute ensuite de l'ammoniaque 1:3 jusqu'à virage au rouge de l'indicateur. Le plomb est alors extrait par une solution chloroformique de dithizone à 0,002%. Il n'est pas nécessaire, comme en colorimétrie, de débarrasser la dithizone de ses produits d'oxydation. La durée de l'extraction est d'une minute pour chaque fraction de 10 ml de solution de dithizone introduite dans l'ampoule. Après séparation des deux phases, l'extrait chloroformique des dithizonates est soutiré et recueilli dans un bécher, forme haute de 100 ml. L'extraction est poursuivie jusqu'à ce que la dithizone conserve sa teinte initiale verte. Deux à trois extractions suffisent généralement. On introduit alors dans le bécher 1 ml d'acide nitrique concentré, on le couvre d'un verre de montre puis on le porte sur plaque métallique portée à la température de 200–250°. Après évaporation complète du chloroforme, le résidu brunâtre est attaqué par 2 ml d'un mélange à volumes égaux d'acide nitrique p.a. à 65% et d'acide perchlorique p.a. à 70%. Le verre de montre n'est retiré qu'au moment où le bécher ne contient plus qu'une trace de liquide. L'évaporation est continuée jusqu'à cessation complète des fumées blanches d'acide perchlorique. Le résidu de minéralisation doit être parfaitement blanc. Ce résidu est finalement dissous dans 5 ml du mélange acétate ammonique 0,5M-acide tartrique 0,1M que nous avons retenu parmi beaucoup d'autres en nous basant sur les deux critères suivants: rapidité de dissolution totale du résidu dans ce milieu; absence d'interférence de la part des métaux extraits par la dithizone à pH 8,5–9 (Co, Ni, Cu, Zn, Cd, Sn, Tl) à l'exception toutefois du thallium dont la présence n'est normalement pas constatée dans les eaux alimentaires. Toutefois, si la présence de thallium est soupçonnée, nous conseillons alors d'utiliser le milieu de Přibil et Zabransky.[10] Suivant ces auteurs le résidu de minéralisation est dissout dans 2,5 ml de sel disodique de l'acide éthylènediaminotétraacétique et 2,5 ml de tampon acétique. La vague du plomb ($E_{1/2} = -1{,}25$ V) est nettement séparée de celle de thallium ($E_{1/2} = -0{,}55$ V). L'étain n'interfère pas en pratique, car il passe de la valence +2 à la valence +4 au cours de la minéralisation. L'étain +4 n'est pas extractible par la dithizone.

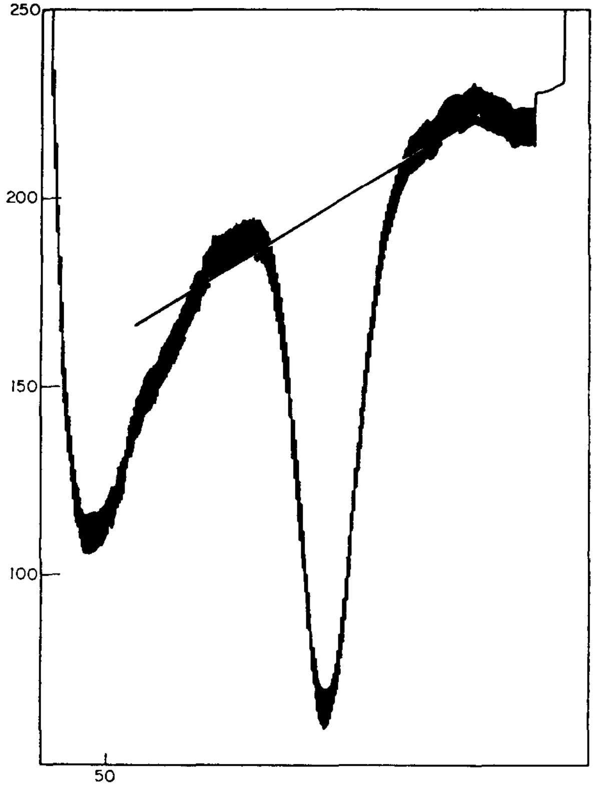

FIG. 1

Polarographie a impulsion

Les polarogrammes ont été enregistrés à partir de solutions obtenues en ajoutant 1 volume de l'acide chlorhydrique 1*M* à 9 volumes d'eau à analyser. Nous avons utilisé la méthode dérivée fournissant des polarogrammes dont la forme est représentée (figure 1). La concentration en plomb de la solution à partir de laquelle ce pic a été enregistré est de 155 μg par litre. Le potentiel du pic se situe aux environs de −0,4 V par rapport à une anode constituée par une nappe de mercure.

Les conditions expérimentales sont les suivantes: 1 goutte de mercure par seconde, la goutte étant détachée artificiellement (autotrig.); condition (*a*); sensibilité $\frac{1}{2} \times \frac{1}{5}$, balayage 1 V en 15 min, intégration 9; conditions (*b*); sensibilité $\frac{1}{4} \times \frac{1}{5}$, balayage 1 V en 7,5 min, intégration 3; conditions (*c*); sensibilite $\frac{1}{2} \times 1$, balayage 1 V en 7,5 min, intégration 3.

Méthode de la goutte pendante

La détermination de la concentration en plomb est effectuée par la technique de l'ajout dosé. La formule suivante permet de calculer la concentration de la substance analysée:

$$C_x = \frac{h_1 C_a v}{V(h_2 - h_1) + h_2 v}$$

où C_x = concentration de la solution analysée
C_a = concentration de l'ajout
h_1 = hauteur du pic fourni par la solution analysée
h_2 = hauteur du pic obtenu après mélange de l'ajout.
V = volume de la solution analysée (22 ml)
v = volume de l'ajout (0,3 ml).

Les conditions opératoires sont les suivantes. On ajoute 2 ml d'acide chlorhydrique concentré à 20 ml d'eau à analyser. Un agitateur magnétique entraîné par un moteur tournant à vitesse constante permet d'obtenir une agitation reproductible. La solution est dégazée pendant 45 min au moyen d'azote désoxygéné. L'électrolyse est effectuée sous un potentiel de $-0{,}65$ V pendant 3 ou 15 min selon les cas. Le balayage anodique (1 V en 6 min) est effectué après avoir laissé la solution au repos pendant 1 min. Le potentiel du pic obtenu est voisin de $-0{,}45$ V. Une solution préparée en ajoutant 2 ml d'acide chlorhydrique concentré à 20 ml d'eau tridistillée fournit un pic de 8 mm à la sensibilité de $1{,}10^{-10}$ A/mm, aprés une électrolyse de 15 min. Cette valeur sera considérée comme "blanc" pour les opérations effectuées à cette sensibilité et pour la même durée de l'électrolyse (échantillons III et IV). Pour les autres opérations la correction de l'essai à blanc est négligeable.

RESUME, DISCUSSION ET CONCLUSIONS

Le tableau I rassemble la totalité des résultats obtenus.

L'oscillopolarographie différentielle ne permet le dosage direct que pour des concentrations en plomb assez nettement supérieures à la limite fixée par l'O.M.S. (50 μg/l.). On obtient en effet pour l'échantillon II une valeur qui souffre de l'imprécision de la courbe d'étalonnage utilisée. La précision obtenue (10 à 15%) est néanmoins suffisante pour un dosage de traces. On peut dès lors admettre que l'oscillopolarographie différentielle permet d'effectuer un dosage direct avec une précision raisonnable lorsque la teneur en plomb dans l'eau est supérieure ou égale à 100 μg/l. Les résultats obtenus par oscillopolarographie et par polarographie à impulsion concordent bien entre eux.

Il importe de souligner également l'avantage essentiel de l'oscillopolarographie différentielle: le plomb introduit comme impureté par les réactifs utilisés est automatiquement soustrait de la teneur en plomb à déterminer.

Les résultats obtenus en utilisant la polarographie à impulsion ont un intérêt pratique assez important. L'examen des courbes d'étalonnage tracées pour la détermination de la teneur en plomb des échantillons I dans les conditions *a* et *b* montre la nécessité de travailler dans les mêmes conditions de balayage et d'intégération. Les pentes des deux droites ne sont pas exactement dans le rapport des sensibilités utilisées. Nous avons vérifié que cette divergence n'est pas due à une proportionnalité imparfaite de l'échelle des sensibilités, mais bien à l'utilisation de conditions de balayage et d'intégration différentes. Notons cependant que les résultats obtenus pour les deux séries de conditions sont concordants, ce qui constitue un argument en faveur de la reproductibilité des mesures effectuées par cette technique.

La droite d'étalonnage utilisée pour déterminer la teneur en plomb des échantillons II, III et IV ne passe pas par l'origine. Ce fait doit être attribué au plomb naturellement présent dans l'acide chlorhydrique utilisé comme milieu de base. Une solution d'acide chlorhydrique 0,1 *N* montre un pic de 12 mm qui correspond avec la valeur déterminée par extrapolation de la droite d'étalonnage jusqu'à concentration nulle en plomb.

De plus, en calculant la concentration en plomb à partir du pic de 12 mm, on trouve une valeur légèrement inférieure à la teneur maximum admise par le fabriquant (produit Merck-*pro analysi*-densité 1,19-N°317-teneur maximum en métaux lourds comme plomb 0,0003% ou environ 3,6 mg/l.)

Les résultats obtenus en utilisant la technique de la goutte pendante sont très nettement différents de ceux obtenus par les deux techniques précédentes, surtout dans le chef des échantillons III et IV. Les divergences ces observées ne peuvent pas s'expliquer avec une certitude absolue. On peut cependant rappeler que la technique de la goutte pendante est assez délicate. Il est nécessaire de reproduire parfaitement une série de conditions expérimentales (agitation, temps d'électrolyse, caractéristiques de la goutte pendante). En outre, elle met en jeu plusieurs phénomènes physico-chimiques différents (réduction, dissolution de la substance réduite dans le mercure, redissolution anodique) qui peuvent, indépendamment l'un de l'autre, être la cause de certaines divergences. Un phénomène parasite gênant est la formation dans le mercure de composés intermétalliques.[8,11,12] Si, généralement, une complication de cette sorte n'apparaît que pour des teneurs en plomb suffisamment élevées (de 10^{-3} à $10^{-4}M$), il n'est pas exclu qu'elle se manifeste également à des concentrations plus faibles et provoque l'apparition de résultats erronés dans le dosage des traces.

Il convient également d'envisager la diffusion du plomb dans le capillaire lorsque le temps d'électrolyse est important. La divergence la plus grande des résultats est observée lorsque le temps d'électrolyse est de 15 min.

Nous pensons que l'application de la méthode à la goutte pendante aux très faibles concentrations (inférieures à $1 \,.\, 10^{-7}M$) devrait faire l'objet d'une étude qui qui sort du cadre de ce travail.

Finalement, il est possible de tirer des diverses comparaisons auxquelles nous nous sommes livrés, les conclusions suivantes. La polarographie à impulsion permet d'obtenir plus rapidement le résultat du dosage que la méthode oscillopolarographique différentielle lorsque la teneur en plomb des échantillons se trouve à proximité de la limite admise par l'O.M.S. En effet, dans ces conditions, l'oscillopolarographie est trop peu sensible pour effectuer un dosage direct et il est alors nécessaire de procéder à une concentration préalable par extraction. La polarographie à impulsion est aussi nettement plus rapide que la méthode de la goutte pendante et les résultats qu'elle permet d'obtenir semblent plus sûrs lorsqu'on considère la complexité des différents phénomènes physico-chimiques sur lesquels se base cette dernière technique. Il semble donc possible d'affirmer que la polarographie à impulsion est actuellement la technique polarographique la plus pratique et la plus générale pour doser le plomb dans les eaux alimentaires jusqu'à la limite de concentration fixée par l'O.M.S. Il faut cependant remarquer que cette méthode nécessite l'utilisation d'un appareillage très complexe et très coûteux.

Summary—It is important to be able to determine lead in drinking water rapidly and accurately. Three polarographic methods are compared: hanging drop polarography, differential oscillographic polarography and pulse polarography. The last seems best.

Zusammenfassung—Es ist wichtig, Blei in Trinkwasser schnell und genau bestimen zu können. Es werden drei polarographische Verfahren verglichen: Polarographie am hängenden Tropfen, Differentialoszillo-polarographie und Impulspolarographie. Am besten schneidet die letzte Methode ab.

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PAPIERCHROMATOGRAPHISCHE UNTERSUCHUNG UND TRENNUNG VON AZODERIVATEN DER CHROMOTROPSÄURE

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Zusammenfassung—Es wurde das papierchromatographische Verhalten einiger Mono- und Bisazoderivate der Chromotropsäure untersucht. Daraus ließ sich ein einfaches und schnelles Verfahren zur Trennung der Mono- und Bisazoderivate entwickeln. Die R_F-Werte für elf verschiedene Mono- und Bisazofarbstoffe werden angegeben. Die Untersuchung einiger Handelspräparate mit dem beschriebenen Verfahren zeigte, daß diese in einigen Fällen aus Gemischen bestehen. Das Verfahren wird zur Reinheitskontrolle von Mono- und Bisazoderivaten der Chromotropsäure empfohlen.

BISAZODERIVATE der Chromotropsäure haben besonders in letzter Zeit zunehmende Bedeutung für photometrische Bestimmungen einiger Metallionen erlangt.[1,2] In einigen Fällen wurden auch die Stabilitätskonstanten der entsprechenden Komplexe bestimmt.[3–9] Der Reinheit der verwendeten Präparate wurde bisher aber nur wenig Aufmerksamkeit gewidmet, obwohl, bedingt durch die relativ schwierige Synthese der Bisazoderivate der Chromotropsäure die Möglichkeit der Verunreinigung durch die entsprechenden Monoazoderivate groß ist. Der Reinheitsgrad der Präparate wurde nahezu ausschließlich elementaranalytisch ermittelt. An Hand dieser Analysenwerte ist aber eine Beurteilung der Reinheit fraglich. Nimmt man z.B. an, daß ein Präparat von Sulfonazo III (2,7-Bis(2'-sulfophenylazo)-chromotropsäure) durch 10% des entsprechenden Monoazoderivates (2-(2'-Sulfophenylazo)-chromotropsäure) verunreinigt ist, so würde man folgende Analysenwerte erhalten: C 38,38% (38,4%); H 2,4 (2,38%); N 7,9% (8,18%); S 18,7% (18,68%). Die entsprechenden Werte für reines Sulfonazo III sind in Klammern angegeben.

Speziell zur Beurteilung von Arsenazo III-Präparaten (2,7-Bis(2'-arsonophenylazo)-chromotropsäure) sind Methoden beschrieben worden, die sich aber nicht ohne weiteres auf andere Bisazoderivate der Chromotropsäure übertragen lassen, da sie genaue Kenntnisse über Absorptionsmaxima und molare Extinktionskoeffizienten der einzelnen Komponenten verlangen.[10,11] Über das papierchromatographische Verhalten von Mono- und Bisazoderivaten der Chromotropsäure sind in der Literatur nur wenig Angaben[12,13] zu finden, obwohl sich diese Methode für eine Reinheitsprüfung besonders eignen sollte.

Aus diesem Grunde haben wir das papierchromatographische Verhalten einer Reihe von Mono- und Bisazoderivaten der Chromotropsäure mit dem Ziel, ein schnell durchführbares und einfaches Verfahren zur Reinheitsprüfung von Handelsprodukten sowie neu dargestellten Substanzen zu finden, näher untersucht.

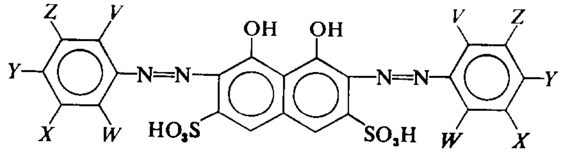
EXPERIMENTELLER TEIL

Reagenzien und Geräte

Die in Tabelle I aufgeführten Farbstoffe I–XI und I*a*–XI*a* wurden nach bekannten Methoden dargestellt. Davon sind V–VII und IX–XI bisher noch nicht beschrieben worden. Über ihre Synthese und ihre Reaktionen mit Metallionen soll in einer gesonderten Veröffentlichung berichtet werden.

In den Kreis der Untersuchungen wurden auch einige Handelspräparate wie 3-(2-Arsonophenylazo)-4,5-dihydroxy-2,7-naphthalindisulfonsäure Dinatriumsalz (identisch mit Farbstoff I*a*), Arsenazo III (identisch mit Farbstoff I), Sulfonazo III (identisch mit Farbstoff II), Nitrosulfonazo III (identisch mit Farbstoff III) und Bromsulfonazo III (identisch mit Farbstoff IV) einbezogen.

TABELLE I.—VERZEICHNIS DER UNTERSUCHTEN AZODERIVATE DER CHROMOTROPSÄURE



lfd.Nr*	Trivialname†	Art der Substituenten
I	Arsenazo III	$V = -\mathrm{AsO(OH)_2}$; $W = X = Y = Z = \mathrm{H}$
II	Sulfonazo III	$V = -\mathrm{SO_3H}$; $W = X = Y = Z = \mathrm{H}$
III	Nitrosulfonazo III	$V = -\mathrm{SO_3H}$; $Y = -\mathrm{NO_2}$; $W = X = Z = \mathrm{H}$
IV	Bromsulfonazo III	$V = -\mathrm{SO_3H}$; $Y = -\mathrm{Br}$; $W = X = Z = \mathrm{H}$
V	Chlorsulfonazo III	$V = -\mathrm{SO_3H}$; $Y = -\mathrm{Cl}$; $W = X = Z = \mathrm{H}$
VI	Dimethylsulfonazo III	$V = -\mathrm{SO_3H}$; $W = Y = -\mathrm{CH_3}$; $X = Z = \mathrm{H}$
VII	Disulfonazo III	$V = X = -\mathrm{SO_3H}$; $W = Y = Z = \mathrm{H}$
VIII	Carboxyazo III	$V = -\mathrm{COOH}$; $W = X = Y = Z = \mathrm{H}$
IX	Sulfocarboxyazo III	$V = -\mathrm{COOH}$; $Y = -\mathrm{SO_3H}$; $W = X = Z = \mathrm{H}$
X	Sulfosalicylazo III	$V = -\mathrm{OH}$; $X = -\mathrm{SO_3H}$; $Z = -\mathrm{COOH}$; $W = Y = \mathrm{H}$
XI	Sulfokresolazo III	$V = -\mathrm{OH}$; $X = -\mathrm{CH_3}$; $Z = -\mathrm{SO_3H}$; $W = Y = \mathrm{H}$

* Die entsprechenden Monoazoverbindungen, die gleichfalls mit untersucht wurden, sind im folgenden mit den laufenden Nummern I*a* bis XI*a* bezeichnet.

† Die Trivialnamen für die Farbstoffe Nr. V, VI, VII, IX, X und XI wurden nach den sich in der Literatur gebildeten Regeln abgeleitet.

Von diesen Farbstoffen wurden 1-proz. wäßrige Lösungen bereitet und mittels einer Mikropipette abgemessene Mengen (im allgemeinen 5–10 μl) auf das Chromatographiepapier aufgetragen. Für Vergleichszwecke dienten 1-proz. wäßrige Lösungen der bei der Synthese verwendeten Diazoniumsalze sowie des Natriumsalzes der Chromotropsäure, von denen ebenfalls 5–10 μl auf das Chromatographiepapier aufgetragen wurden. Als Fließmittel fanden folgende Lösungen Anwendung:

Fließmittel Nr. 1: n-Butanol:Eisessig:Wasser (2:1:1)
Fließmittel Nr. 2: 10-proz. wäßrige Ammoniaklösung
Fließmittel Nr. 3: Wasser
Fließmittel Nr. 4: 0,1 n Essigsäure
Fließmittel Nr. 5: 0,1 n Salzsäure
Fließmittel Nr. 6: 0,1 n Schwefelsäure
Fließmittel Nr. 7: 1,0 n Salzsäure.

Als Chromatographiepapier standen die Kurzkeilstreifen der Firma VEB Spezialpapierfabrik Niederschlag/Erzgeb. zur Verfügung. Die Type FN 14/K, ein säuregewaschenes, mittelschnell laufendes Papier, erwies sich als besonders geeignet. Die Entwicklung der Chromatogramme erfolgte im Chropagerät* Nr. K-3-15 der Firma VEB Glaswerke Illmenau.

Ergebnisse

Die Ergebnisse der Versuche sind in den Tabellen II–IV zusammengestellt. Die dort mitgeteilten R_F-Werte sind Mittelwerte aus wenigstens drei Versuchen.

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* Eingetragenes Warenzeichen der Firma.

TABELLE II.—CHROMATOGRAPHIE DER FARBSTOFFE I UND I*a* MIT VERSCHIEDENEN FLIEẞMITTELN

Fließmittel Nr.	R_F-Werte I	R_F-Werte I*a*	Bemerkungen
1	0,85	0,88	Dauer 5 Stdn. Farbstoff I zeigt sehr diffuse Zone. Im Gemisch schlechte Trennung beider Farbstoffe.
2	0,94	0,93	Im Gemisch keine Trennung beider Farbstoffe; Dauer 1,5 Stdn.
3	0,82	0,86	Im Gemisch schlechte Trennung beider Farbstoffe; Dauer 2 Stdn.
4	0,62	0,72	Farbstoff I zeigt sehr verwaschene Zone. Im Gemisch schlechte Trennung beider Farbstoffe; Dauer 2 Stdn.
5	0,50	0,62	Gute Trennung; Dauer 2 Stdn.
6	0,45	0,57	Gute Trennung; Dauer 2 Stdn.
7	0,42	0,53	Gute Trennung; Dauer 2 Stdn.

TABELLE III.—CHROMATOGRAHIE DER FARBSTOFFE I BIS XI UND I*a* BIS XI*a*

Farbstoff Nr*	R_F-Wert	Farbe	Bemerkung
I	0,50	violett	
I*a*	0,62	rotviolett	
II	0,81	blauviolett	
II*a*	0,69	rot	
III	0,61	blauviolett	
III*a*	0.55	rotviolett	
IV	0,60	blauviolett	
IV*a*	0,07	rotviolett	
V	0,66	blauviolett	
V*a*	0,58	rotviolett	
VI	0,91	blauviolett	
VI*a*	0,81	rotviolett	
VII	0,88	blauviolett	Im Gemisch gehen die Zonen beider Farbstoffe unmittelbar ineinander über, sind aber gut zu unterscheiden
VII*a*	0,85	rot	
VIII	0,0	blau	
VIII*a*	0,28	rot	
IX	0,28	blauviolett	
IX*a*	0,60	rot	
X	0,32	blauviolett	
X*a*	0,52	rotviolett	
XI	0,33	blauviolett	
XI*a*	0,47	rotviolett	

Fließmittel Nr. 5; Papier FN 14/K; Dauer 2 Stdn.

* Die einander entsprechenden Bisazofarbstoffe (römische Ziffern) und Monoazofarbstoffe (römische Ziffern mit Index *a*) stehen in der Tabelle untereinander.

TABELLE IV.—ERGEBNISSE DER PAPIERCHROMATOGRAPHISCHEN UNTERSUCHUNG EINIGER HANDELSPRODUKTE.

Produkt	R_F-Wert	Farbe	Intensität der Färbung*
3-(2-Arsonophenylazo)-4,5-dihydroxy-2,7-naphthalindisulfonsäure Dinatriumsalz	0,62	rotviolett	st
Uranon *p*	0,62	rotviolett	st
	0,52	violett	schw
Arsenazo III	0,62	rotviolett	m
	0,52	violett	st
	0,00	braunviolett	m
Sulfonazo III	0,81	blauviolett	st
	0,14	bräunlich	schw
Bromsulfonazo III	0,72	rot	schw
	0,66	rot	schw
	0,60	blauviolett	st
	0,07	rotviolett	schw
Nitrosulfonazo III	0,73	rot	schw
	0,61	blauviolett	schw
	0,19	gelblich	schw
	0,09	rotviolett	schw

Fließmittel Nr. 5; Papier; FN 14/K; Dauer 2 Stdn.

* Die Intensität der Färbung wurde visuell abgeschätzt. Die Abkürzungen bedeuten: st = stark; m = mittel; schw = schwach.

DISKUSSION

Da *a priori* ein einfaches und schnell durchführbares Verfahren zur Reinheitsprüfung von Bisazoderivaten der Chromotropsäure angestrebt wurde, kam als Methode nur die Chromatographie auf Rundfiltern oder Kurzkeilstreifen in Frage. Gegenüber der Chromatographie auf Rundfiltern bietet die Kurzkeilstreifenmethode den Vorteil besser reproduzierbarer Ergebnisse. Außerdem können durch Chromatographie auf Keilstreifen bekanntlich auch Substanzen mit sehr ähnlichen R_F-Werten gut getrennt werden.[14] Vorversuche zeigten, daß sich für eine schnelle Trennung das Papier FN 14/K besonders eignet. Mit dem schneller laufenden Papier FN 11/K erfolgt in einigen Fällen nur eine ungenügende Trennung, während mit dem langsamer laufenden Papier FN 16/K zwar eine gute Trennung, jedoch auf Kosten einer längeren Entwicklungsdauer zu erzielen war.

Die ersten Versuche wurden mit dem Fließmittel Nr. 1 durchgeführt, welches sich bei der papierchromatographischen Trennung von Farbstoffen verschiedenster Konstitution bewährte.[15] Mit diesem Fließmittel lassen sich jedoch die Mono- und Bisazoderivate der Chromotropsäure nur schlecht trennen; außerdem dauert die Entwicklung der Chromatogramme relativ lange (etwa 5 Stdn.). Wie aus der Tabelle II zu ersehen ist, führt die Verwendung verdünnter Lösungen von Mineralsäuren zu einer raschen und guten Trennung der Mono- und Bisazoderivate der Chromotropsäure. Dabei beruht die Trennung aber wohl kaum auf einer Verteilung zwischen zwei Phasen, sondern auf einer unterschiedlichen Adsorption der verschiedenen Komponenten am Papier, was schließlich auch die Form der Flecken andeutet. Während der vordere Rand der Bogenzonen immer sehr scharf ist, erscheint die hintere Begrenzung (dem Startpunkt zugewandt) immer mehr oder weniger verschwommen. Trotzdem aber lassen sich die R_F-Werte dieser Zonen auch bei der relativ kurzen Laufstrecke des Fließmittels von etwa 10 cm bemerkenswert gut reproduzieren. Dagegen übt Art und Weise der Auftragung der Farbstoffe auf das Papier in einigen Fällen beträchtlichen Einfluß auf die Trennung aus. Dies ist besonders bei Verwendung der Fließmittel Nr. 1, 3 und 4, d.h. solche, die keine oder nur schwache Säuren enthalten, der Fall oder wenn die Farbstoffe entweder als freie Säuren oder als Salze aufgetragen werden. Wahrscheinlich beruht dies auf der unterschiedlichen Adsorption der verschiedenen Dissoziationsformen der Farbstoffe. Es ist deshalb zu empfehlen, die Farbstoffe entweder als freie Säuren aufzutragen oder wenn dies nicht möglich ist (z.B. bei Handelsprodukten), die aufgetragenen Farbstoffe durch kurzes Räuchern mit Salzsäure in die freien Säuren zu überführen. Da von vornherein anzunehmen war, daß das Fließmittel Nr. 5(0,1 n Salzsäure) weder das Papier zerstört (wichtig für die Dokumentation der Ergebnisse) noch Reaktionen mit den Farbstoffen eingeht, wurde nur noch das Fließmittel Nr. 5 verwendet.

Wie aus Tabelle III hervorgeht, lassen sich somit alle in Tabelle I aufgeführten Mono- und Bisazoderivate der Chromotropsäure gut trennen. In den Fällen mit nur geringen Unterschieden der R_F-Werte zwischen Mono- und Bisazoderivat, können diese trotzdem gut an ihrer unterschiedlichen Färbung erkannt werden. Bisazofarbstoffe, die in Orthostellung zur Azogruppe Carboxyl- oder Hydroxyl-Gruppen besitzen, zeigen nur kleine R_F-Werte. Die entsprechenden Monoazofarbstoffe besitzen beträchtlich größere R_F-Werte und sind gut von den entsprechenden Bisazofarbstoffen zu trennen. Hier nicht näher geschilderte Versuche zeigten, daß diese Bisazofarbstoffe mit dem Fließmittel Nr. 2 große R_F-Werte liefern. Dann erfolgt jedoch nur eine schlechte Trennung der Mono- und Bisazofarbstoffe.

Das Fließmittel Nr. 5 diente auch zur Untersuchung einiger Handlesprodukte. Wie aus Tabelle IV hervorgeht, bestehen diese in einigen Fällen aus Gemischen. So enthält das Monoazoderivat Uranon *p* auch das Bisazoderivat, während das ensprechende Bisazoderivat Arsenazo III durch den Monoazofarbstoff verunreinigt ist. Eine halbquantitative Abschätzung der Verhältnisse ist schwierig, da die Monoazoderivate gegenüber den Bisazoderivaten im allgemeinen nur etwa halb so große molare Extinktionskoeffizienten besitzen. Gleichstarke Färbungen der Zonen würde somit etwa einem Verhältnis von Bisazoderivat zu Monoazoderivat wie 1:2 entsprechen. Da die Mono- und Bisazoderivate aber unterschiedlich gefärbt sind, läßt sich ein Verhältnis nur schwer abschätzen.

Auf den Chromatogrammen der Handelsprodukte lassen sich in einigen Fällen noch weitere Zonen erkennen. Durch Chromatographie von frisch bereiteten wie auch von gealterten Lösungen der bei der Synthese verwendeten Diazoniumsalze war festzustellen, daß diese Zonen Zersetzungsprodukten der Diazoniumsalze entsprechen. Chromotropsäure selbst besitzt mit dem Fließmittel Nr. 5 einen R_F-Wert von 0,80. Sie läßt sich nur dann als Verunreinigung nachweisen, wenn die Farbstoffe andere R_F-Werte besitzen, da diese sonst die relativ schwache Färbung die die Chromotropsäure bei Besprühen mit Eisen(III)-chloridlösung liefert, überdecken.

Das beschriebene Verfahren wird zur Reinheitskontrolle von Bisazoderivaten der Chromotropsäure empfohlen. Dabei ist es vorteilhaft, daß die Entwicklung der Chromatogramme nur 2 Stdn. dauert, so daß bereits während der Synthese eine Beurteilung der Qualität des Produkts möglich ist. Das analytische Verfahren ist nach allem auch ohne weiteres auf andere, hier nicht untersuchte Bisazoderivate der Chromotropsäure übertragbar.

Herrn Prof. Dr. K. Issleib möchten wir für die Bereitstellung von Institutsmitteln sowie für sein förderndes Interesse an dieser Arbeit danken. Herrn Prof. Dr. L. Sommer, Institut für Analytische Chemie der J. E. Pukyné Universität Brno, ČSSR, sind wir für die freundliche Überlassung einiger Handelsprodukte zu Dank verpflichtet.

Summary—The paper chromatographic behaviour of some mono- and bis-azo derivatives of chromotropic acid was studied, leading to a simple and rapid method for separation of mono- and bisazo derivatives. The R_F-values of eleven different mono- and bisazo dyes are given. The investigation of some commercial preparations with the method described shows that these are mixtures in some cases. The method is recommended for the control of purity for mono- and bisazo derivatives of chromotropic acid.

Résumé—On a étudié le comportement chromatographique sur papier de quelques dérivés mono- et bisazo de l'acide chromotropique, conduisant à une méthode simple et rapide pour la séparation des dérivés mono- et bisazo. On donne les valeurs R_F de onze colorants mono- et bisazo différents. L'étude de quelques préparations commerciales par la méthode décrite montre que dans quelques cas celles-ci sont des mélanges. On recommande la méthode pour le contrôle de pureté des dérivés mono- et bisazo de l'acide chromotropique.

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SPECTROPHOTOMETRIC EXTRACTIVE TITRATIONS—V*

THEORETICAL APPROACH TO TITRATION OF A SINGLE CATION

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Summary—The general equation of the titration curve for spectrophotometric extractive titrations is derived. The graphical location of the end-point is assumed and the significance of the general equation is discussed. Simple formulas for threshold pH and for sensitivity are obtained. An increased selectivity of spectrophotometric extractive titrations in comparison with that of the usual spectrophotometric extractive methods is demonstrated.

RECENTLY a technique for the determination of microgram amounts of metals, based on extractive titration followed spectrophotometrically without any sampling of aqueous or organic phase, has been developed.[1] In order to make the method applicable to reagents other than dithizone, which was used in the earlier work, and because of the need to predict theoretically the optimum conditions of titration, a mathematical treatment of the spectrophotometric extractive titration has been developed.

GENERAL EQUATION OF THE TITRATION CURVE

At any point during the spectrophotometric extractive titration of metal ion M^{M+} in the presence of metal ion N^{N+} with chelating agent HA, the absorbance, A, of the organic phase is given by:

$$A = l(\varepsilon_{MA_M} \cdot [MA_M]_{org} + \varepsilon_{NA_N} \cdot [NA_N]_{org} + \varepsilon_{HA} \cdot [HA]_{org}) \qquad (1)$$

where $[MA_M]_{org}$, $[NA_N]_{org}$, and $[HA]_{org}$ are concentrations of the metal chelates and free HA in the organic phase, ε_{MA_M}, ε_{NA_N} and ε_{HA} are the molar absorptivities of the species indicated and l is the light path-length. It is assumed throughout that equilibrium has been reached. Then the extraction constant[2] may be used to express the concentrations in equation (1). The extraction constants are defined by:

$$K_M = \frac{[MA_M]_{org}[H]^M}{[M][HA]^M_{org}} \text{ and } K_N = \frac{[NA_N]_{org}[H]^N}{[N][HA]^N_{org}}, \qquad (2)$$

where [H] is the equilibrium concentration of hydrogen ion. Here and elsewhere the charges of ions are omitted for the sake of simplicity.

If $K_M > K_N$, the equilibrium concentration of free titrant $[HA]_{org}$ is determined by K_M and

$$[HA]_{org} = [H]\left(\frac{[MA_M]_{org}}{K_M \cdot [M]}\right)^{1/M}. \qquad (3)$$

The equilibrium concentration, $[MA_M]_{org}$, must be derived having regard to the

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* Part IV—*Talanta*, 1967, **14**, 731.

fact that the reaction of the chelating agent with metal ion M will not generally be quantitative under the conditions of titration, *i.e.*,

$$[\mathrm{MA_M}]_{\mathrm{org}} = E\frac{c_{\mathrm{HA}}}{M}, \tag{4}$$

where E is the degree of reaction and c_{HA} is the total concentration of the chelating agent in the organic phase at the given stage of titration (calculated according to the volume of the organic phase, V_{org}, present in the titration cell at the start of the titration).

The equilibrium concentration $[\mathrm{NA_N}]_{\mathrm{org}}$ and the equilibrium concentrations [M] and [N] in the aqueous phase may be derived from the mass balances:

$$[\mathrm{NA_N}]_{\mathrm{org}} = \frac{1}{N}(c_{\mathrm{HA}} - [\mathrm{HA}]_{\mathrm{org}} - M[\mathrm{MA_M}]_{\mathrm{org}}), \tag{5}$$

$$[\mathrm{M}] = c_{\mathrm{M}} - \frac{[\mathrm{MA_M}]_{\mathrm{org}} \cdot V_{\mathrm{org}}}{V}, \tag{6}$$

$$[\mathrm{N}] = c_{\mathrm{N}} - [\mathrm{NA_N}]_{\mathrm{org}} \cdot \frac{V_{\mathrm{org}}}{V}, \tag{7}$$

where c_{M}, c_{N} denote the initial concentrations of metal ions in the aqueous phase of volume V.

Flaschka,[3] who dealt with the theory of chelometric photometric titrations in the aqueous phase, introduced the useful idea of the equivalent ratio of titrant to metal ion, a. For a metal ion of valency $M+$ the equivalent ratio is given by:

$$a = \frac{c_{\mathrm{HA}} V_{\mathrm{org}}}{M c_{\mathrm{M}} V}. \tag{8}$$

Solution of equations 1–8 gives the general equation of the titration curve in parametric form:

$$\mathrm{A} = l.\Bigg\{\varepsilon_{\mathrm{MA_M}} c_{\mathrm{M}} Ea \frac{V}{V_{\mathrm{org}}} + \varepsilon_{\mathrm{HA}} \mathrm{B_M} M \left(\frac{Ea}{1 - Ea}\right)^{1/M} + \varepsilon_{\mathrm{NA_N}} . \left(\frac{V}{V_{\mathrm{org}}}\right)^{(M+N)/M} \left(\frac{Ea}{1 - Ea}\right)^{N/M} \frac{c_{\mathrm{N}} K_{\mathrm{M}}^{(M-N)/M}}{Q + \left(\frac{Ea}{1 - Ea} \cdot \frac{V}{V_{\mathrm{org}}}\right)^{N/M} K_{\mathrm{M}}^{(M-N)/M}}\Bigg\}, \tag{9a}$$

$$a = Ea + \left(K_{\mathrm{M}} \frac{V_{\mathrm{org}}}{V}\right)^{(M-N)/M} \frac{N}{M} \frac{V}{V_{\mathrm{org}}} \left(\frac{Ea}{(1 - Ea)}\right)^{N/M} \times \frac{c_{\mathrm{N}}/c_{\mathrm{M}}}{Q + \left(\frac{EaV}{(1 - Ea)V_{\mathrm{org}}}\right)^{N/M} K_{\mathrm{M}}^{(M-N)/M}} + \left(B_{\mathrm{M}} \frac{Ea}{1 - Ea}\right)^{1/M}, \tag{9b}$$

where $Q = K_{\mathrm{M}}/K_{\mathrm{N}}$ and B_{M} is the ratio

$$[\mathrm{H}]^M . \left(\frac{V_{\mathrm{org}}}{V}\right)^{N-1} |K_{\mathrm{M}} . c_{\mathrm{M}}{}^M . M^M| .$$

Values of A and a for various values of the product Ea ($0 < Ea < 1$) may be calculated so it is possible to obtain the whole titration curve for given initial concentrations [H], c_M and c_N, assuming that K_M, K_N, V and V_{org} are known, (Figs. 1–5).

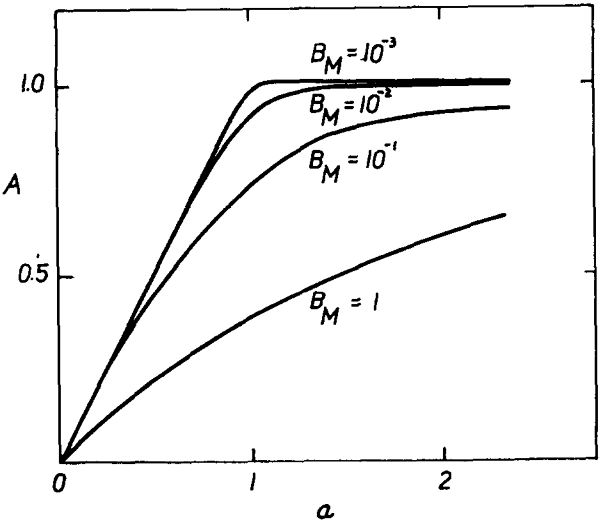

FIG. 1.—Titration of univalent cation.

$\varepsilon_{MA_M} l c_M = 1$; $\frac{V_{org}}{V} = 1$; $c_N = 0$; $\varepsilon_{HA} = 0$.

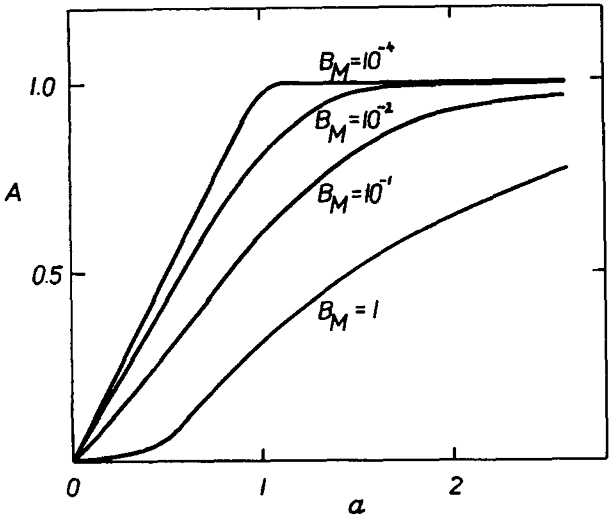

FIG. 2.—Titration of bivalent cation.

$\varepsilon_{MA_M} l c_M = 1$; $\frac{V_{org}}{V} = 1$; $c_N = 0$; $\varepsilon_{HA} = 0$.

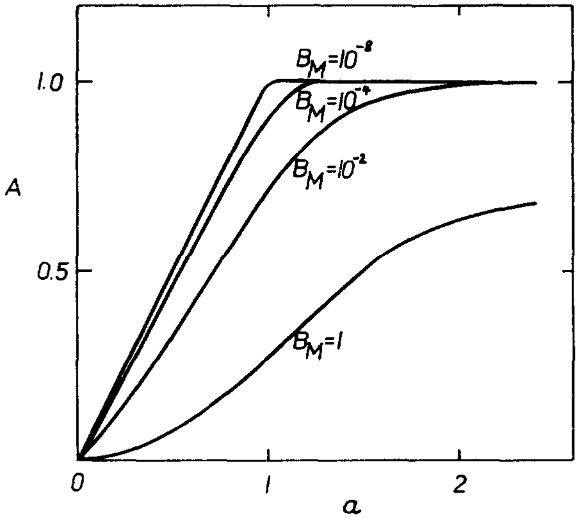

FIG. 3.—Titration of tervalent cation.

$\varepsilon_{MA_M} lc_M = 1$; $\frac{V_{org}}{V} = 1$; $c_N = 0$; $\varepsilon_{HA} = 0$.

DISCUSSION

Location of the end point

If the metal ion M is to be titrated after its preliminary separation from all other metal ions extractable with the titrant, the equation of the titration curve contains only the terms concerning the properties of reagent and of metal chelate MA_M. Further simplification may be achieved by assuming that the titration is followed at the wavelength of maximum absorbance of the chelate MA_M, at which in most cases the absorbance of the unreacted reagent is negligible. In such a case it is usual[3] to establish the end-point as the abscissa of the intersection of two straight lines, one of them passing through the origin and through the point when half of the titrant has been added, the other passing through the points when 50 and 150% excess of the titrant has been added.

It is in principle possible to continue the titration far beyond the end-point, and so to obtain points on the curve where the slope is essentially zero. This simplifies the considerations derived below, because the second straight line may be parallel to the axis on which the volume of titrant is plotted, and pass through the point of maximum absorbance.

Threshold pH

The prediction of the proper conditions for successive spectrophotometric extractive titration requires a knowledge of the pH range of the solution being analysed which will give the results to the accuracy demanded. Straight lines can be drawn through the experimental points of the titration curve in terms of the general equations (9*a*) and (9*b*). The first line is drawn through points $a = 0$, $A = 0$ and $a = 0{\cdot}5$, $A = A_{0{\cdot}5}$; the second has zero slope and goes through the point $A = l\varepsilon_{MA_M} C_M V/V_{org}$, as $a \rightarrow \infty$, where all the metal ion M is completely extracted. If it is assumed that the permissible analytical error is $<1\%$ it may be concluded that the degree of reaction $E_{0.5}$ at $a = 0.5$ must be >0.991. Introduction of these values into general equations (9*a*) and (9*b*) (when $c_N = 0$, $\varepsilon_{HA} = 0$) gives the critical values of B_M and equations for the minimum satisfactory or threshold pH shown in Table I.

TABLE I.—CRITICAL VALUES IN THE TITRATION OF METAL ION M

Charge on the metal ion	Critical B_M value	Threshold pH*
1	2.338×10^{-3}	$2.63 - \log K_M - \log c_M$
2	1.321×10^{-5}	$2.14 - \frac{\log K_M}{2} - \log c_M$
3	4.723×10^{-8}	$1.97 - \frac{\log K_M}{3} - \log c_M$
4	2.125×10^{-10}	$1.82 - \frac{\log K_M}{4} - \log c_M$

* Supposing that $V = V_{org}$.

It must be noted that the errors considered above are positive, but negative errors may arise, *e.g.*, if titrant absorbs at the same wavelength as the chelate.

The highest pH value suitable for titration depends on the ease of hydrolysis of the metal ion in aqueous solution and the dissociation of the organic reagent, which limits the validity of equations (1)–(9), as in substoichiometric separations by extraction.[2] Usually the knowledge of the threshold pH is the most significant, because near this pH the titration is most selective.

Sensitivity

The sensitivity of most methods of trace analysis depends on the variability of the procedure blank, but this factor will not be considered in the discussion below, which deals with the limitations of the method.

The sensitivity is dependent on two factors; (*i*) the extraction process, and (*ii*), the measurement of absorbance.

(*i*) The least determinable amount of metal ion may be computed from the equation for threshold pH, if it is borne in mind that the maximum value of threshold pH is limited by at least three conditions: (*a*) the general equations of the titration curve, (9*a*) and (9*b*) must be valid, *i.e.*, the dissociation of the reagent in the aqueous phase must be negligible—$V[A] \ll [HA]_{org}V_{org}$; this rule is fulfilled for hydrogen ion concentrations lower than $pK_{HA} + \log P_{HA} + \log V_{org}/V$, where K_{HA} is the dissociation constant and P_{HA} the distribution coefficient of the reagent; (*b*) the threshold pH must be lower than that at which the precipitation of hydroxide of the metal ion titrated begins; (*c*) the threshold pH must be lower than that at which the precipitation of hydroxides of metals other than the titrated one begins, otherwise losses due to co-precipitation may be expected.

These conditions may be conveniently expressed as

$$pH_t < pH_{crit}, \tag{10}$$

where pH_t is the threshold pH and pH_{crit} is the lowest value of pH given by condition

a, b, or c. Formulae for the lowest determinable concentration of metal ion $(c_M)_{min}$ were calculated from equation (10) and Table I, and are shown in Table II.

TABLE II.—SENSITIVITY OF THE TITRATION

Charge on the metal ion	Log minimum concentration suitable for titration
1	$2{\cdot}63 - \log K_M - \mathrm{pH}_{crit}$
2	$2{\cdot}14 - \frac{1}{2}\log K_M - \mathrm{pH}_{crit}$
3	$1{\cdot}97 - \frac{1}{3}\log K_M - \mathrm{pH}_{crit}$
4	$1{\cdot}82 - \frac{1}{4}\log K_M - \mathrm{pH}_{crit}$

(*ii*) When the spectrophotometric extractive titration is followed at the wavelength of maximum absorbance of the chelate formed, it is desirable to determine at least five distinct points on the first branch of the titration curve, so the absorbance due to metal chelate formed compared to that of all the metal present must be at least five times that which is reliably measurable by the spectrophotometer used. Then the least determinable amount of metal M is given by

$$(c_M)_{min} = \frac{5A_{min}V_{org}}{\varepsilon_{MA_M}lV} \tag{11}$$

where A_{min} is the minimum absorbance measurable.

From equations (10) and (11), it is evident that the theoretical sensitivity of spectrophotometric extractive titration is lower than that of the usual extractive spectrophotometric methods. Nevertheless, it must be noted that in spectrophotometric extractive titrations so far developed[4,5] the real sensitivity was limited mainly by the reproducibility of the procedure blank.

Selectivity

When the analysed solution contains metal ion M together with metal ion N which also reacts with the titrant, it is not possible to simplify the basic equations (9*a*) and (9*b*). The shape of the titration curve in this case is that shown in Figs. 4 and 5. It is evident that the slope of the branch of the curve after the end-point is not generally zero. The end-point may be located by extrapolating the straight lines going through points A_0, $A_{0{\cdot}5}$ and $A_{2{\cdot}5}$, $A_{3{\cdot}0}$.

From the line before the equivalence point, if $A_0 = 0$, then $A_1 = 2A_{0{\cdot}5}a$, and from the line after the equivalence point,

$$A_1 = 2(A_{3{\cdot}0} - A_{2{\cdot}5})a + A_{2{\cdot}5} - 5(A_{3{\cdot}0} - A_{2{\cdot}5}).$$

Rearrangement gives an equation for a and since at the equivalence point a should be 1·00, the error Δ, expressed as equivalents, is given by

$$\Delta = \frac{A_{2{\cdot}5} - 5(A_{3{\cdot}0} - A_{2{\cdot}5})}{2(A_{0{\cdot}5} - A_{3.0} + A_{2{\cdot}5})} - 1 \tag{12}$$

where the subscripts denote the stoichiometric ratio of added titrant to total metal M present.

Calculation of the appropriate A_i from equations (9*a*) and (9*b*) for a given system enables the systematic error to be predicted. These calculations, however, are very

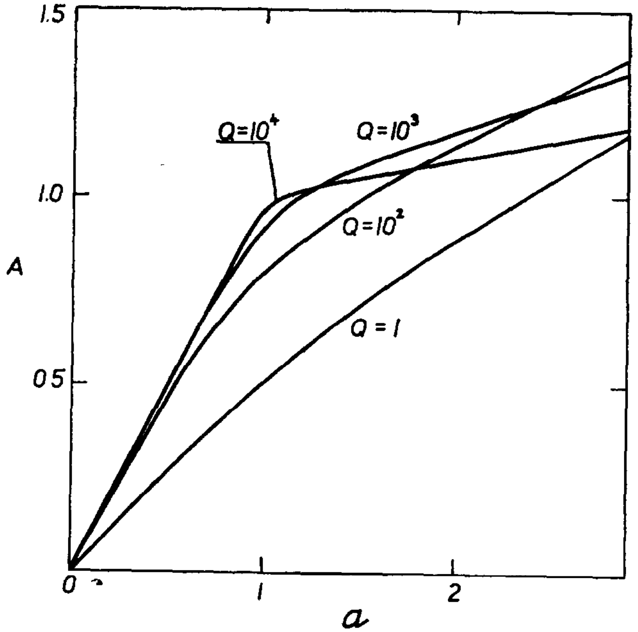

FIG. 4.—Titration of univalent cation M in the presence of tenfold excess of univalent cation N.

$\varepsilon_{MA_M} l c_M = 1$; $\varepsilon_{MA_M} = 5\varepsilon_{NA_N}$; $B_M = 10^{-3}$; $\frac{V_{org}}{V} = 1$, $\varepsilon_{HA} = 0$; $K_M = 10^6$.

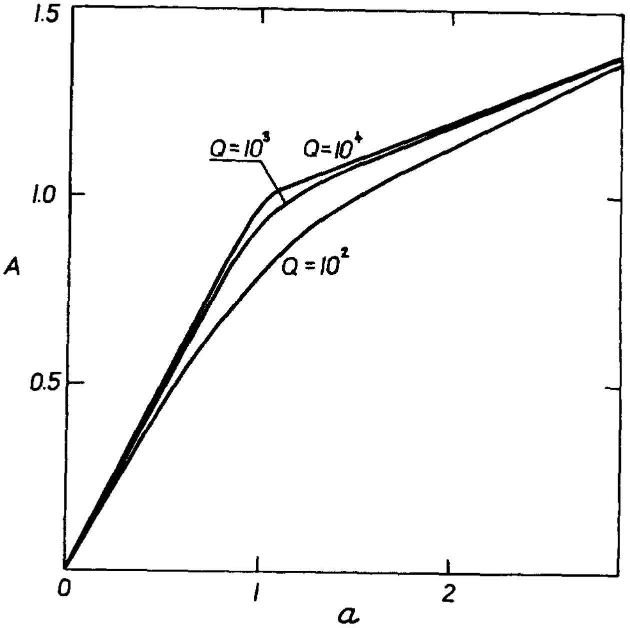

FIG. 5.—Titration of bivalent cation M in the presence of tenfold excess of bivalent cation N.

$\varepsilon_{MA_M} l c_M = 1$; $\varepsilon_{MA_M} = 5\ \varepsilon_{NA_N}$; $B_M = 10^{-4}$; $\frac{V_{org}}{V} = 1$; $\varepsilon_{HA} = 0$; $K_M = 10^6$.

tedious as no general expression for *Ea* as a function of equivalent ratio *a* is possible, so they are not presented here.

It is much more important to compare the selectivity of spectrophotometric extractive titration with the usual spectrophotometric analytical method where an excess of extractive agent is used. From the data used in preparing Fig. 4 it was concluded that approximately $+2\%$ error arises in the presence of tenfold excess of metal ion N which forms a chelate with a molar absorptivity one fifth that of the metal titrated, at the wavelength chosen, if $Q = 10^3$. In the case of a spectrophotometric extractive method where an excess of chelating extractant is used, 99% extraction of metal ion M is secured at concentrations of hydrogen ion lower than

$$[\mathrm{H}] = \frac{K_\mathrm{M} \cdot [\mathrm{HA}]_\mathrm{org}}{99} .$$

If $Q = 10^3$, the distribution ratio of metal ion N is

$$\frac{[\mathrm{NA_N}]_\mathrm{org}}{[\mathrm{N}]} = \frac{K_\mathrm{N} \cdot [\mathrm{HA}]_\mathrm{org}}{[\mathrm{H}]} \simeq 10^{-3} \cdot 10^2 = 0{\cdot}1.$$

If $c_\mathrm{N} = 10 c_\mathrm{M}$ and $5\varepsilon_{\mathrm{NA_N}} = \varepsilon_{\mathrm{MA_M}}$, a 19% positive error will arise.

In order to diminish the error to the level obtained by titration, only 1·5% extraction of metal N may be allowed, which means that the extraction constant of metal ion N must not exceed the value

$$K_\mathrm{N} = \frac{1{\cdot}5[\mathrm{H}]}{98{\cdot}5[\mathrm{HA}]_\mathrm{org}} = 1{\cdot}5 \times 10^2.$$

In other words, the ratio $K_\mathrm{M}:K_\mathrm{N}$ must be $>6{\cdot}7 \times 10^3$.

It is evident that the spectrophotometric extractive titration is more selective than the usual spectrophotometric method.

CONCLUSION

It has been shown that the spectrophotometric extractive titration of a single cation is theoretically less sensitive than the usual spectrophotometric method with extractive separation, but the titration is more selective. It is concluded that the use of spectrophotometric extractive titration for the determination of microgram quantities of metals is advantageous.

Zusammenfassung—Die allgemeine Gleichung der Titrationskurve spektrophotometrischer extraktiver Titrationen wird abgeleitet. Es wird graphische Ermittlung des Endpunktes angenommen und die Bedeutung der allgemeinen Gleichung diskutiert. Man erhält einfache Formeln für die pH-Schwelle und die Selektivität. Es wird eine verbesserte Empfindlichkeit spektrophotometrischer extraktiver Titrationen demonstriert, verglichen mit den üblichen spektrophotometrischen Extraktivverfahren.

Résumé—On établit l'équation générale de la courbe de titrage pour les titrages spectrophotométriques par extraction. On admet la localisation graphique du point de fin de dosage et discute la signification de l'équation générale. On obtient des formules simples pour le seuil de pH et pour la sensibilité. On démontre une sélectivité accrue des titrages spectrophotométriques par extraction par comparaison à celle des méthodes spectrophotométriques par extraction usuelles.

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DETERMINATION OF SCANDIUM BY ATOMIC ABSORPTION

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Summary—A comprehensive study has been made of the determination of scandium by atomic absorption. In addition to the instrumental variables such as flame-height, slitwidth and lamp current, a number of solution variables have been studied including the effect of anions (chloride, sulfate, nitrate, and fluoride), organic solvents, and other metals on the determination of scandium. Standard conditions have been established for the detection of minor amounts of scandium in a wide variety of materials including complex alloys of iron, nickel, aluminium, magnesium, and the rare earths.

HOLLOW-cathode lamps for scandium have become commercially available in the past two years and recently Manning[1] has suggested several wavelengths which can be used for the determination of scandium by atomic absorption. No comprehensive study has previously been made, however, of experimental conditions necessary for the determination of scandium in actual samples. This paper reports a study of instrumental operating parameters in addition to an investigation of the effect of anions, organic solvents, and other metals on the determination of scandium in complex alloys of aluminium, magnesium, iron, nickel and misch metal.

EXPERIMENTAL

Apparatus

A Techtron Model AA-4 Atomic Absorption Spectrophotometer with a nitrous oxide burner head and a R106 photomultiplier tube was used for this study. The recorder was a Sargent SRL model; the scandium hollow cathode lamp was manufactured by Atomic Spectral Lamps Pty. Ltd. The operating parameters were: acetylene pressure variable; nitrous oxide pressure 16 psi; lamp current 10 mA; burner height setting 7; damping setting for maximum stability D.

RESULTS AND DISCUSSION

Slitwidth and sensitivity

The effect of varying the slitwidth was studied for the three most sensitive resonance wavelengths of scandium, by aspirating a 50-ppm aqueous solution (of the chloride). As shown in Fig. 1, varying the slitwidth had comparatively little effect on the sensitivity; however, a maximum was noted in two cases at about 75 μ.

Typical working curves are shown in Fig. 2. Sensitivity, expressed as the concentration of scandium producing 1% absorption, is 0·8 ppm at 3911·8 Å, and 1 ppm at 3907·5 and 4023·7 Å.

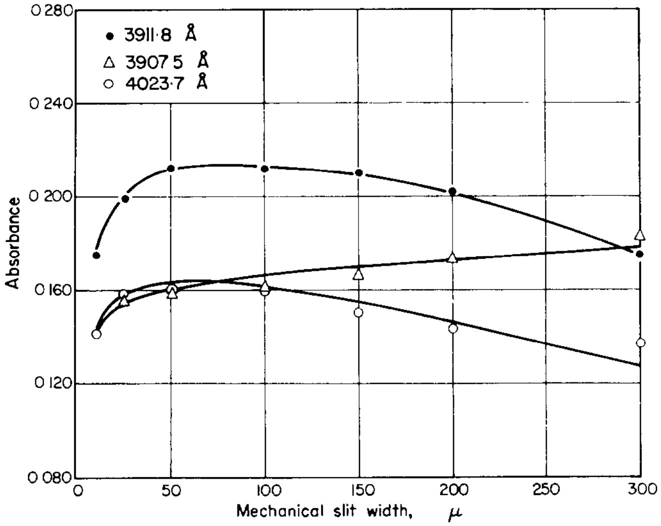

FIG. 1

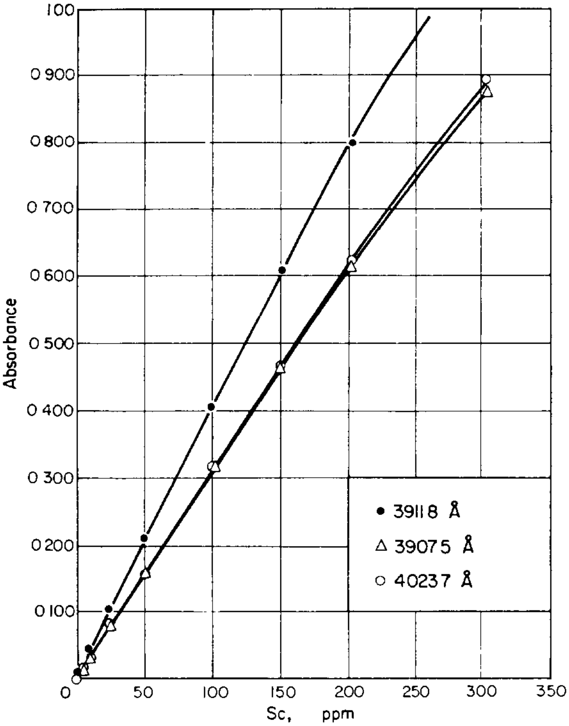

FIG. 2

Anion interference

The effect of anions on the determination of scandium by atomic absorption is shown in Table I. The absorption at 3911·8 Å by a 50-ppm solution of scandium (as chloride) was measured at a slitwidth of 75 μ. Fluoride ion produces serious interference, probably owing to precipitation of scandium fluoride, hence it must be absent from samples analyzed by this technique. It is evident that while moderate

TABLE I.—THE EFFECT OF ANIONS ON THE DETERMINATION OF SCANDIUM

Anion added	Concn. of anion, *ppm*	Absorbance
None	—	0·250
Chloride	100	0·250
	10000	0·224
	40000	0·200
Nitrate	100	0·250
	10000	0·227
	85000	0·208
Sulfate	100	0·198
	2500	0·222
	5000	0·254
	15000	0·280

amounts of chloride and nitrate have only a minor effect on the absorbance of scandium, if samples are to be aspirated which contain major amounts of these ions, standards must also have similar compositions. The effect of sulfate is more important than that of nitrate or chloride, and it is of particular note that 5000 ppm of sulfate produce almost no interference while 100 ppm produce a significant decrease in sensitivity.

Organic solvents

A study was made of the effect of organic solvents on the determination of scandium by atomic absorption. Standard instrument operating conditions were used, and aqueous samples containing 50 ppm of scandium (as chloride) and varying amounts of acetone, methanol and ethanol were measured. Results are shown in Table II. It can be postulated that the decrease in sensitivity found for 50 and 75% acetone solutions is due either to increased ionization of scandium atoms or oxide formation in the highly luminous flame.

TABLE II.—THE EFFECT OF ORGANIC SOLVENTS ON THE DETERMINATION OF SCANDIUM

Solvent	% *v/v*	Absorbance
H_2O	100	0·243
Acetone	10	0·285
	25	0·280
	50	0·152
	75	0·059
Methanol	10	0·280
	25	0·305
	50	0·350
	75	0·430
Ethanol	10	0·302
	25	0·331
	50	0·370
	75	0·425

Effect of potassium and ammonium ions

Potassium[2] and ammonium[3] ions are frequently used in atomic absorption spectroscopy to increase sensitivity by decreasing flame ionization of the metal to be determined. The effect of these cations on the determination of scandium is shown in

TABLE III.—THE EFFECT OF POTASSIUM AND AMMONIUM IONS ON THE DETERMINATION OF SCANDIUM

Ion added	Concn. *ppm*	Absorbance
None	—	0·233
Potassium	1000	0·276
	2000	0·276
	5000	0·281
	10000	0·292
Ammonium	1000	0·268
	5000	0·300
	10000	0·310

Table III. All solutions contained 50 ppm of scandium as the chloride. It should be noted that although 1000 ppm of potassium enhance the absorbance significantly, more has little additional effect.

Cation effects

The effect of various cations was studied by measuring the absorbance of solutions containing 25 ppm of scandium and varying concentrations of other elements as chlorides and is shown in Table IV. In general, more oxidizing flame conditions are required for maximum absorbance as the amount of other cations present increases. Exceptions were noted in the case of rare earths or aluminium where no change in the gas ratio is necessary. In fact, in the presence of lanthanum, more fuel-rich conditions are desirable. The effect of 1000 ppm of potassium in suppressing the interference of cations is also shown in Table IV. Lanthanum was tried as an interference–suppressant but unsuccessfully; of the ions tested, only potassium was effective in this respect.

It is evident from the data in Table IV that for precise determinations of scandium it is necessary to synthesize standards which are similar to the samples. This is particularly true for the determination of small amounts of scandium in the presence of major amounts of other elements. Particular note should be taken of the fact that potassium significantly reduces the interference of aluminium.

The influence of burner height on cation interference was determined by measuring the absorbance at different heights in the flame of solutions containing 25 ppm of scandium and varying amounts of Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{2+}, and Ni^{2+}, all added as chlorides. Results shown in Table V indicate that the interference of Cr^{3+}, Fe^{3+}, Co^{2+} and Ni^{2+} in scandium measurement is more severe in the higher regions of the flame but that aluminium interference is reduced. Measurement in the higher regions of the flame resulted in a 50% reduction in sensitivity and necessitated the use of extremely fuel-rich conditions, markedly increasing the amount of deposits collecting in the burner and causing it to become plugged more frequently.

Application to specific alloy systems

No certified reference samples are available which contain known amounts of scandium in the range 0·01–1%; consequently, a series of samples was prepared by dissolving scandium-free materials and adding to them known amounts of scandium. The materials selected for study were NBS 86c (Al-base, 7·9% Cu, 1·5% Zn, 0·9% Fe), NBS 171 (Mg-base, 3·0% Al, 1·0% Zn, 0·5% Mn), NBS 349 (Ni-base, 19·5% Cr,

TABLE IV.—THE EFFECT OF OTHER CATIONS ON THE DETERMINATION OF SCANDIUM

Cation added	Concn. ppm	Absorbance	
		No KCl added	1000 ppm K added as KCl
None	—	0·110	0·123
Al^{3+}	2500	0·023	0·115
	25000	0·012	0·033
Ti^{4+}	2500	0·092	0·146
	6250	0·085	0·135
Cr^{3+}	2500	0·112	0·133
	25000	0·088	0·110
	125000	0·031	0·043
Fe^{3+}	2500	0·110	0·125
	25000	0·060	0·106
	125000	0·016	0·030
Co^{2+}	2500	0·119	0·136
	25000	0·077	0·129
	125000	0·027	0·045
Ni^{2+}	2500	0·128	0·136
	25000	0·100	0·090
	125000	0·035	0·035
Cu^{3+}	2500	0·132	0·150
	25000	0·104	0·112
	125000	0·087	0·102
Y^{3+}	2500	0·148	0·155
	12500	0·168	0·165
La^{3+}	2500	0·155	0·159
	25000	0·162	0·172
Pr^{3+}	2500	0·152	0·160
	6250	0·157	0·165
Nd^{3+}	2500	0·155	0·157
	6250	0·158	0·162
Th^{4+}	2500	0·138	0·160
	12500	0·152	0·168
UO_2^{2+}	2500	0·116	0·139
	6250	0·118	0·129

TABLE V.—THE INFLUENCE OF BURNER HEIGHT ON CATION INTERFERENCE

Burner height setting \ Cation added		Absorbance				
	None	Al^{3+} 2500 *ppm*	Cr^{3+} 25000 *ppm*	Fe^{3+} 25000 *ppm*	Co^{2+} 25000 *ppm*	Ni^{2+} 25000 *ppm*
7	0·110	0·022	0·083	0·051	0·061	0·076
9	0·106	0·023	0·064	0·028	0·029	0·040
11	0·093	0·029	0·033	0·020	0·017	0·015
13	0·082	0·033	0·018	—	—	—
17	0·065	0·045	—	—	—	—
20	0·063	0·053	—	—	—	—
21	0·062	0·053	—	—	—	—

TABLE VI.—LIMITING SENSITIVITY FOR SCANDIUM BY ATOMIC ABSORPTION

Sample	Concentration of scandium, %
NBS 86c (Al-base)	0·01
NBS 171 (Mg-base)	0·005
NBS 349 (Ni-base)	0·02
NBS 160a (Fe-base)	0·005
Misch metal	0·001

14·0% Co, 4·0% Mo, 3·0% Ti, 1·2% Al), NBS 160a (Fe-base, 18·7% Cr, 14·1% Ni, 2·8% Mo, 1·6% Mn) and misch metal. The limiting sensitivity for scandium in these materials, expressed as that concentration of scandium in the metal sample which will produce 1% absorption, is shown in Table VI. The controlling factor in most cases was the viscosity of the solution aspirated which was caused by the high salt content. This high salt content also caused the burner to become blocked rapidly by deposition of salts, an effect that could be reduced, with only a slight loss in sensitivity, by dilution with an equal volume of ethanol.

The preparation of samples for analysis is summarized below.

Aluminium-base alloys. Dissolve with hydrochloric acid (1 + 1), adding 30% hydrogen peroxide as needed, then evaporate just to dryness on a hot-plate. Add water, warm to dissolve salts, cool, and dilute to volume after adding sufficient ethanol and potassium chloride to give final concentrations of 50% v/v ethanol and 1000 ppm of potassium.

Magnesium-base alloys. Dissolution procedure and final solution conditions as for aluminium-base materials except that no peroxide is required.

Nickel-base alloys. Dissolve the sample in *aqua regia*, and evaporate just to dryness on a hot-plate. Add sufficient hydrochloric acid to give a final concentration of 10% v/v, heat to dissolve salts, cool and dilute to volume after adding ethanol and potassium chloride as for aluminium-base alloys.

Iron-base alloys. Identical procedure to that for nickel-base materials, except that no hydrochloric acid is added before dilution of the sample.

Misch metal. Dissolve samples in dilute hydrochloric acid, cool, add sufficient potassium chloride to make the final potassium concentration 1000 ppm. Dilute to volume but do not add ethanol.

For the most precise work the standards should have very similar compositions to the samples, the permissible variation in concentration of any component being limited to ±10%. The standard addition method is particularly useful, as shown by the results in Table VII.

TABLE VII.—SCANDIUM DETERMINED BY STANDARD ADDITION TECHNIQUE

Sample	Sc added, %	Sc recovered, %
NBS 86c	0·100	0·110
NBS 171	0·050	0·051
NBS 349	0·100	0·098
NBS 160a	0·050	0·050
Misch metal	0·100	0·098

Résumé—On a effectué une étude complète du dosage du scandium par absorption atomique. En plus des variables instrumentales comme la hauteur de flamme, la largeur de fente et l'intensité de la lampe, on a étudié un certain nombre de variables de la solution, incluant l'influence d'anions (chlorure, sulfate, nitrate et fluorure), de solvants organiques et d'autres métaux sur le dosage du scandium. On a établi des conditions types pour la détection de faibles quantités de scandium dans une large variété de produits comprenant des alliages complexes de fer, nickel, aluminum, magnésium, et les terres rares.

Zusammenfassung—Die Scandiumbestimmung durch Atomabsorption wurde eingehend untersucht. Außer den instrumentellen Parametern wie Flammenhöhe, Spaltbreite und Lampenstrom wurden einige Parameter der Lösung untersucht, wie Anioneneinfluß (Chlorid, Sulfat, Nitrat, Fluorid), organische Lösungsmittel, Fremdmetalle. Standardbedingungen zur Bestimmung kleiner Scandiummengen in vielen verschiedenen Materialien wie komplizierten Legierungen von Eisen, Nickel, Aluminium, Magnesium und seltenen Erden wurden ermittelt.

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ADSORPTION OF CATIONS FROM FORMIC ACID SOLUTIONS ON STRONG ACID CATION-EXCHANGE RESIN

SEPARATION OF ZIRCONIUM FROM THORIUM AND FROM GALLIUM

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Summary—The adsorption of Pb(II), Cu(II), Bi(III), Cd(II), Mn(II), Co(II), Ga(III), Y(III), Zr(IV) and Th(IV) from aqueous solutions of formic acid on cation-exchanger Dowex 50W-X8 has been studied. Electrophoretic measurements have also been made. Possible separations are suggested and discussed. Zirconium may be quantitatively separated from thorium and from gallium.

FORMIC acid is known to form complexes with many metal ions,[1-4] and use has been made of some of them to facilitate separations. Korkisch and Urabay[4] have shown that uranium can be separated from copper, lead and gadolinium on anion-exchange resin with 1:9 formic acid–methanol for the first two separations and 1:9 formic acid–isobutanol for the last. However, only a few studies on the adsorption of metal formate complexes on cation-exchange resins have been reported[2,5,6] and the present work aimed at a more detailed study of this field, resulting in some interesting possibilities for separations. Among these was the quantitative separation of zirconium from thorium and from gallium.

EXPERIMENTAL

Reagents

Ion-exchange resin. Air-dried Dowex 50W-X8 (100–200 mesh) in the Na^+ form was used, converted into the H^+ form by washing with $3M$ hydrochloric acid, washing with water, and drying in air.

Standard metal solutions, $0{\cdot}05M$. Prepared from the chlorides or nitrates of the metals, dissolved in demineralized water. When necessary, the minimum amount of hydrochloric or nitric acid was added to prevent hydrolysis.

Apparatus

For the electrophoretic studies, an instrument made by Eastern Laboratory Instruments (India) was used.

Determination of the metal ions

All the metal ions were determined titrimetrically with standard $0{\cdot}002M$ EDTA, suitable indicators being used.

Determination of distribution coefficients

The batch equilibrium method was used to determine the coefficients according to the relationship

$$K_d = \frac{\mu\text{g of element per g of resin}}{\mu\text{g of element per ml of solution}}$$

To 0·5 ml of test solution and 24·5 ml of formic acid of the desired molarity ($0{\cdot}01$–$1{\cdot}0M$) in a 100-ml conical flask was added 0·5 g of air-dried resin in the H^+ form, and the mixture was agitated in a water-bath at 30 ± 1° for 3 hr. The mixture was then filtered, and the element determined in the filtrate.

Separation of zirconium and thorium

A slurry of 2·2 g of resin in water was poured into a 1·05-cm diameter column, giving a height of 5 cm. The resin was converted into the H^+ form by washing with about 50 ml of 3*M* hydrochloric acid, then washed with water. The column was saturated by passage of 50 ml of 0·05*M* formic acid, and then the mixture of zirconium and thorium was added (in 0·05*M* acid). The zirconium was eluted by passing more 0·05*M* formic acid through the column, at a flow rate of 14 ml/min. Rather more eluent was run through than was required, then the column was washed with 10 ml of water. The thorium was eluted with 3·0*M* sulphuric acid at a flow-rate of 1·5 ml/min. The effluents were collected separately, and the metal ions determined.

TABLE I.—QUANTITATIVE SEPARATION OF ZIRCONIUM AND THORIUM

Volume of effluent		Zirconium		Thorium	
Eluent A, 0·05*M* HCOOH	Eluent B, 3·0*M* H_2SO_4	taken, *mg*	found, *mg*	taken, *mg*	found, *mg*
120	215	0·32	0·32	1·03	0·97
125	180	0·41	0·40	0·57	0·58
125	215	0·41	0·40	1·14	1·15
125	180	0·61	0·60	0·57	0·58
125	215	0·61	0·61	1·14	1·14
125	180	0·82	0·82	0·57	0·60
125	215	0·82	0·82	1·14	1·15
140	215	1·02	1·03	1·14	1·15

Separation of zirconium and gallium

A slurry of 1 g of air-dried resin in water was poured into a column of diameter 0·9 cm, and converted into the H^+ form. Mixtures of zirconium and gallium in 0·05*M* formic acid were passed through the column at a flow-rate of 3·5 ml/min. The gallium was strongly adsorbed and the zirconium passed straight through. Gallium was subsequently eluted with 1·3*M* hydrochloric acid at a flow-rate of 1·5 ml/min.

TABLE II.—QUANTITATIVE SEPARATION OF ZIRCONIUM AND GALLIUM

Volume of effluent		Zirconium		Gallium	
Eluent A, 0·05*M* HCOOH	Eluent B, 1·3*M* HCl	taken, *mg*	found, *mg*	taken, *mg*	found, *mg*
200	220	1·53	1·52	3·76	3·76
215	205	2·04	2·04	2·63	2·62
225	220	2·55	2·55	3·76	3·76
225	200	2·55	2·55	1·88	1·88

Electrophoresis

Whatman No. 1 paper sheets were cut into strips 4 × 36 cm, and the strips were allowed to saturate in the tank with the formic acid solution. The metal ions were applied at the middle of the paper, the tank was closed and a potential of 200 V was applied for 3 hr. The strips were then dried in an oven, and the metal ions detected by dipping into suitable reagent solutions.

RESULTS AND DISCUSSION

The adsorption behaviour observed for the various elements is summarized in Fig. 1 as a plot of the distribution coefficient K_d *vs.* molarity of formic acid. *Total ads.* denotes an element not detected in the solution after equilibration with the resin. The results of the electrophoresis experiments are summarized in Table III. It is clear that positively charged complexes are formed for all the ions with the exception of zirconium, which seems to have a negative charge.

Magnesium, *zinc*, *bismuth* and *yttrium* are all partially adsorbed, and the variation in K_d with formic acid concentration suggests that more than one ionic species is present for each metal ion. The electrophoretic experiments would seem to support this.

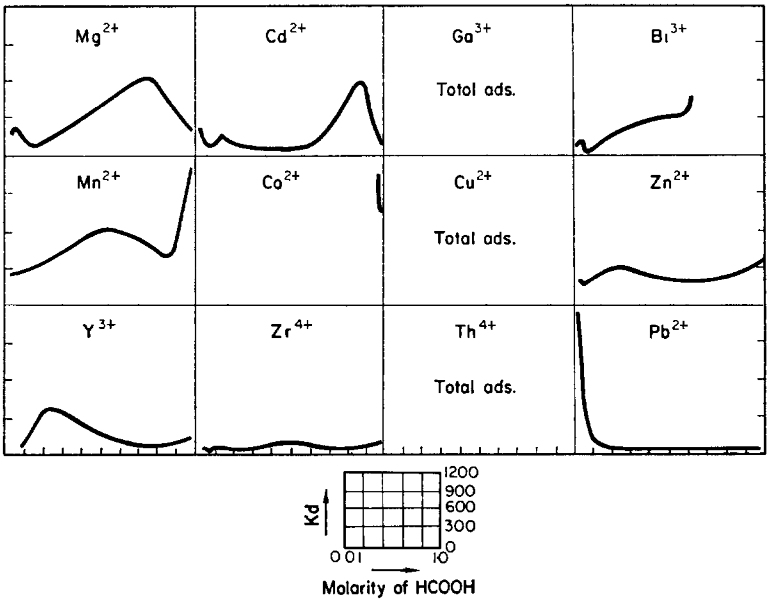

FIG. 1.—Adsorption of cations from HCOOH solutions.

Lead behaves very differently from *manganese* and *cadmium* which are rather strongly adsorbed, and a separation of lead from these two would seem possible, particularly in more concentrated formic acid solutions.

Cobalt, *copper*, *gallium and thorium* are all very strongly adsorbed over the whole range of acid concentrations studied.

Zirconium, *thorium* and *gallium* have already been discussed, and the separations studied (Tables I and II). The behaviour of zirconium in acid solutions (nitric, perchloric, and sulphuric) has been studied by Lister and McDonald[7] who found evidence for both anionic and cationic species containing zirconium. The adsorption and electrophoresis studies reported here would support the assumption that anionic species exist in formic acid solutions.

Acknowledgement—The authors express their gratitude to A. R. Kidwai and S. M. F. Rahman for research facilities and for their interest in the work.

Zusammenfassung—Die Adsorption von Pb(II), Cu(II), Bi(III), Cd(II), Mn(II), Co(II), Ga(III), Y(III), Zr(IV) und Th(IV) aus wäbrigen Ameisensäurelösungen an dem Anionenaustauscher Dowex 50W-X8 wurde untersucht. Auch elektrophoretische Messungen wurden gemacht. Trennungsmöglichkeiten werden vorgeschlagen und diskutiert. Zirkonium kann quantitativ von Thorium und Gallium getrennt werden.

TABLE III.—ELECTROPHORETIC STUDIES OF CATIONS IN FORMIC ACID SOLUTIONS

[HCOOH]	Distance moved by the cation from the centre of the paper towards cathode (—) or anode (+), *cm*								
Cations	1·0*M*	0·9*M*	0·7*M*	0·5*M*	0·2*M*	0·1*M*	0·05*M*	0·02*M*	0·01*M*
Cu(II)	8·6 → — (0·0–3·5) → —	12·0 → —	(9–12·0) → —	11·0 → —	11·2 → —	5·2 → —	5·2 → —	2·5 → —	1·7 → —
Bi(III)	(0·0–0·7) → +	(0·0–3) → —	(0·0–3·5) → —	(0·2–2·0) → —	(0·0–1·9) → —	(0·0–1·7) → —	0·0 → ±	(0·0–2·0) → —	(0·0–2·0) → —
Cd(II)	9·0 → —	12·5 → —	12·0 → —	11·0 → —	13·5 → —	(4·9–8·9) → —	(4·5–10·5) → —	4·0 → —	1·7 → —
Pb(II)	9·0*T* → —	11·5*T* → —	(11–13·2) → — 0·3 → —	11·5 → —	11·7*T* → —	6·2*T* → —	5·2*T* → —	(2·3 — 4·7*T*) → —	2·3 → —
Zn(II)	(9·7–14·5) → —	12·5 → —	(11·0–16·7) → — 0·0 → ±	(10·4–13·0) → —	(11·5–17·5) → —	(6·1–10·5) → —	(4·5–13) → —	(1·2–11·0) → —	2·7 → —
Mn(II)	10·5 → —	11·7 → —	(12·5–16·0) → —	(8·5–12·5) → —	(11·5–16·5) → —	10·0 → —	(2·5–9·0) → —	(1·0–11·0) → —	(1·7–3·4) → —
Co(II)	11·2 → —	12·5 → —	12·5 → —	12·0 → —	13·5 → —	6·5 → —	(5·2–11·5) → —	(1·5–4·5) → —	(0·7–13·2) → —
Mg(II)	9·8 → —	12·5 → —	(13·5–17·5) → —	(11·2–13·0) → —	(5·5–10·2) → —	(4·1–8·0) → —	(0·3–2·6) → —	(2–3·0) → —	(0·7–3·4) → —
Y(III)	10·7 → —	12·7 → —	12·6 → —	(12·6–15·1) → —	(8–15) → —	(7–9) → —	(3·5–7·0) → —	(2·3–5·5) → —	(2·1–4·7) → —
Th(IV)	6·3 → —	7·5 → —	(4·5–10·2) → —	(5·5–10·5) → —	(4·0–9·5) → —	(1·8–6·8) → —	(0·3–4·5) → —	(0·5–2·5) → —	(0·0–1·7) → —
Zr(IV)	2·5 → + (0·0–4·2) → —	(0·0–2·5) → —	2·7 → + (0·00–3·5) → —	(0·0–0·7) → + (0·0–6·0) → —	(0·0–2·2) → —	(0·0–2·5) → —	(0·0–1·5) → —	0·0 → ±	(0·0–2·6) → —
Ga(II)	(1·7–9·2) → —	(4·2–10·5) → —	(7·0–11·0) → —	(5·5–10·5) → —	(0·0–9·0) → —	(2·5–6·7) → —	(0·0–5·0) → —	(1·11–5·5) → —	(0·0–3·1) → —

T = Tailing.

Résumé—On a étudié l'adsorption de Pb(II), Cu(II), Bi(III), Cd(II), Mn(II), Co(II), Ga(III), Y(III), Zr(IV) et Th(IV) sur l'échangeur cationique Dowex 50W-X8 à partir de solutions aqueuses d'acide formique. On a également effectué des mesures électrophorétiques. On suggère des séparations possibles et en discute. On peut séparer quantitativement le zirconium du thorium et du gallium.

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COLORIMETRIC DETERMINATION OF NITRITES WITH *p*-DIAMINODIPHENYLSULPHONE–DIPHENYLAMINE AS REAGENT

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Summary—Diaminodiphenylsulphone–diphenylamine is used in a new colorimetric method for the determination of nitrite over a range of 0·1–2·5 mg/l. at pH 1·8 and 0·22–0·4 mg/l. at pH about 0·1. The coloured solutions are stable, follow Beer's law and are suitable for determination of traces by visual comparison. The method is selective and neither chlorine nor nitrogen trichloride gives similar colour reactions.

ALTHOUGH many investigations have been made to find an adequate method for determination of small amounts of nitrites and their precursors, the generally accepted and applied method is the colorimetric method based on the Griess reaction,[1] as developed by Ilosvay about 90 years ago. The original method has been re-examined and modified by several authors.[2–7] The Griess–Ilosvay procedure modified by Weston[4] predominated for many years, but more recently the modification by Rider and Mellon[5] has become the standard procedure. A review by Sawicki *et al.*[8] which compares 52 spectrophotometric methods for nitrite determinations concludes that "better analytical methods are needed for the analysis of nitrites and their precursors". The advantages of the method presented here are high sensitivity, accuracy, wide range, lack of photosensitivity, conformity to Beer's law, and simplicity. This method is specially suited for field use, because the reaction can be carried out at the site, and the reading taken in the laboratory several days or even weeks later.

EXPERIMENTAL

Reagents

p-*Diaminodiphenylsulphone, DDS.* A commercial (Fluka) sample was purified by recrystallization from hot 50% aqueous ethanol. The reagent was used as a 0·2% solution in 96% ethanol containing 20% w/v of citric acid.

Diphenylamine solution. A 0·04% solution in 96% ethanol containing 20% w/v of citric acid.

Perchloric acid (60–70%).

Standard nitrite stock solution. A 0·3% solution of sodium nitrite, made alkaline with a few drops of 1*M* sodium hydroxide. The solution is standardardized with permanganate and diluted with nitrite-free water to give a standard solution containing 2·46 g of sodium nitrite/1., corresponding to 500 ppm of nitrogen. The solution should be stored in a refrigerator; chloroform may be added as a preservative. Working standards are prepared by suitable dilution with nitrite-free water.

Other reagents and solvents used were reagent grade.

Procedures

At pH 1·8. Mix equal volumes of DDS and diphenylamine solutions to give a mixed reagent solution, which remains colourless and stable for several months. Add 5 ml of the mixed reagent solution to an equal volume of sample solution containing 0·5–12·5 mg of nitrite nitrogen and mix. Allow to stand at room temperature for at least 1 hr and measure the absorbance of the solution in a 1-cm cell at 450 mμ against a blank of equal volumes of water and 20% citric acid in ethanol. Determine the nitrite content of the sample from a calibration curve prepared by treating known amounts of nitrite according to the procedure. Determinations can be made with up to 10 ppm nitrite nitrogen without dilution, as no precipitation occurs even at high concentrations (0·2-cm cell).

The colour is fully developed within an hour. Beer's law is obeyed and the molar absorptivity is 15×10^3 mole^{-1}. cm^2.

At pH 0·1. Add 0·75 ml of DDS solution to a 10-ml sample containing 0·2–4 μg of nitrite nitrogen and mix. Let the solution stand for 3–10 min and then add 0·75 ml of diphenylamine solution, mix and allow to stand at room temperature for about 30 min. Add 1 ml of perchloric acid and mix. Maximum colour intensity is obtained in 4–5 hr after addition of the acid. Measure the absorbance in a 1-cm cell at 520 mμ against a blank of a mixture of 10 ml of water, 1·5 ml of 20% citric acid in ethanol and 1 ml of perchloric acid. Determine the nitrite content of the sample by means of a calibration curve, prepared in the usual way.

The colour intensity remains constant for several weeks in darkness or several days in daylight. Beer's law is followed. The molar absorptivity is 55×10^3 mole^{-1} cm^2.

The absorption spectra of the reaction products in both working procedures are shown in Fig. 1.

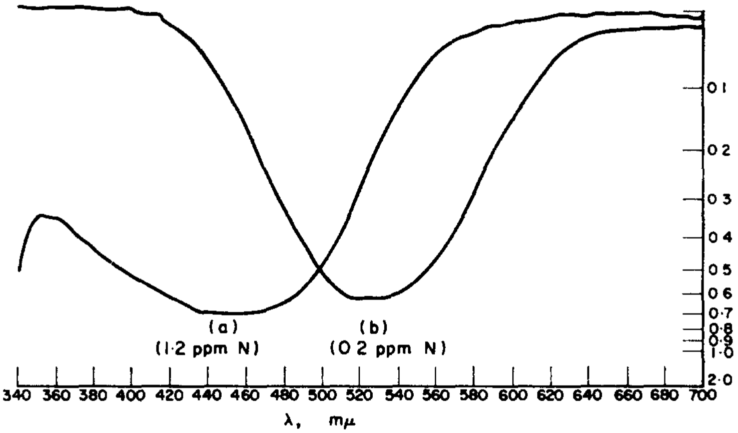
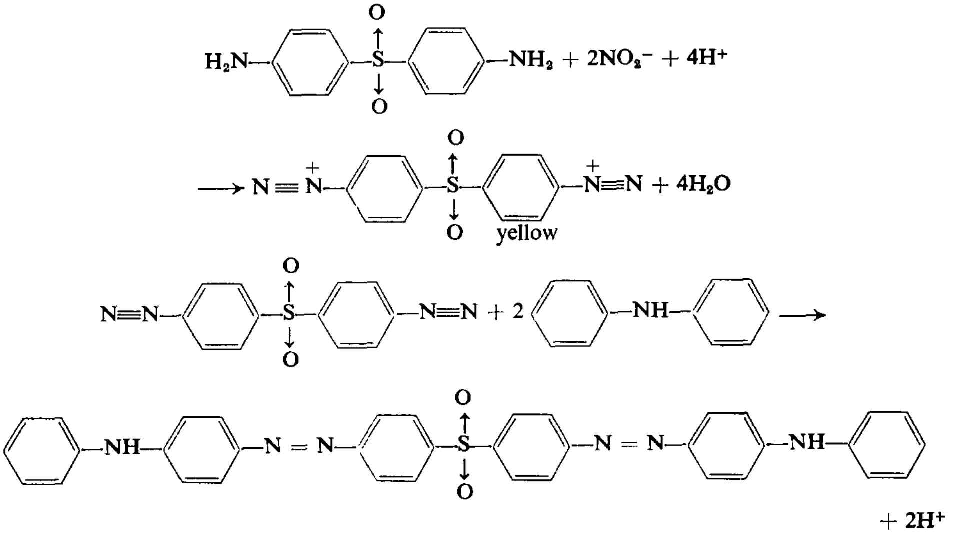


FIG. 1.—Absorption spectra of the reaction products, (*a*) at pH 1·8, (*b*) at pH 0·1.

RESULTS AND DISCUSSION

Colour reaction

The reaction is summarized by the following equations:



The final reaction product is probably bisdiphenylamino-4,4′-diazodiphenylsulphone, an acid–base indicator which changes its colour between pH 0·6 and 1·2, from apricot yellow to reddish violet; it is stable under acid conditions. The acid and base forms have different molar absorptivities at λ_{max}, which accounts for the difference in sensitivity between the two methods.

Factors which affect the colour development

According to the equations above, 2 moles of nitrite react with 1 of DDS and 2 of diphenylamine, but experimentally it has been found that the successful determination needs a large excess of the diazotizing agent and some excess of the coupling agent.

The most favourable diazotizing conditions were found at a pH of about 1·8. This pH is yielded by the high concentration of citric acid in the reagents and it is therefore not normally necessary to adjust the pH of the samples. When volumes of 0·5, 1·0, 2·0, and 5 ml of DDS solution were added to 10-ml samples with concentrations between 1 and 5 ppm nitrite nitrogen, and the absorbance of the pale yellow diazotization product (at 378 mμ) was measured as a function of time, it was found that maximum colour development was obtained in 3 min and the colour was stable for 10 min. Afterwards the mixture became turbid. The diazotization experiments were repeated at temperatures between 10 and 40°, without effect on the results. The coupling process is also independent of temperature between 10 and 40°, but the colour develops more quickly at higher temperatures. It was found that the order of addition of reagents did not affect the colour development.

TABLE 1.—ACCURACY AND PRECISION OF DETERMINATION OF NITRITE BY PROCEDURE AT pH 1·8

	N found,	
N taken, *ppm*	average, *ppm*	max. dev., *ppm*
0·100	0·098	0·005
0·250	0·251	0·008
0·500	0·505	0·015
1·00	1·00	0·02
2·00	1·99	0·05
2·50	2·53	0·07

Two different working procedures have been described, differing only in the amount of the reagents and the pH. The first procedure is simple, precise and relatively quick. It is applicable to larger quantities of nitrites (0·1–2·5 ppm as nitrogen). The second procedure is more sensitive and thus suitable for determination of minute quantities of nitrites. As little as 1 ppM nitrite nitrogen can be estimated visually by comparison with standards (1 ppM = 1 in 10^9).

Procedure at pH 1·8

Table I shows the average value and maximal deviation for five consecutive nitrite determinations.

Procedure at pH 0·1

Full colour development is obtained slowly at room temperature under strongly acidic conditions. Readings can only be taken several hours after starting the determination. A standard solution of nitrite (0·2 ppm N) was analysed by the procedure, (*a*) at room temperature, and (*b*) by starting at room temperature and heating the reaction mixture without the acid for 5 min in a boiling water-bath and cooling immediately. Readings were first taken after 45 min and thereafter every hr.

The results (Fig. 2) show that heating increases the rate of the reaction at the expense of sensitivity. The accuracy and precision are not affected, so heating is recommended if speed is desired and the loss of sensitivity is not important.

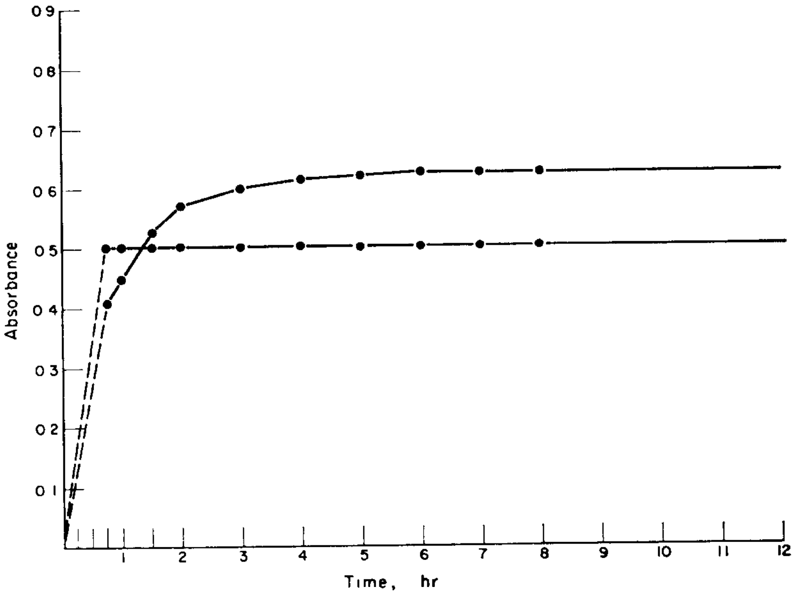


FIG. 2.—Absorbance as function of time for procedure at pH 0·1, (*a*) at room temperature, (*b*) with heating, 0·2 ppm N.

Diazotization and coupling can procede simultaneously if DDS and diphenylamine are added simultaneously or as a mixture, but the reaction is quicker when the recommended procedure is followed. The colour can also be developed by the simultaneous addition of the reagents and the acid in the proportions indicated, but the colour development is slower and the intensity approximately 15% less than in the normal procedure; the reagent mixture is less stable and becomes discoloured after a few days.

After the addition of the acid (in the recommended procedure) a further increase in intensity occurs and the full colour development is obtained only after several hr. The colour turns reddish-violet below pH 0·6 but the maximal intensity is obtained in higher acid concentration.

The effect of different inorganic acids was examined. The best results were obtained with perchloric acid, but almost the same intensity is obtained with 25% hydrochloric acid. The intensity and colour stability are lowest in sulphuric acid medium.

Table II shows the results for five consecutive nitrite determinations on each of 7 standard solutions of nitrite.

TABLE II.—ACCURACY AND PRECISION OF PROCEDURE AT pH 0·1

	N found,	
Taken, *ppm*	average, *ppm*	max. dev., *ppm*
0·020	0·019	0·002
0·040	0·039	0·001
0·080	0·081	0·003
0·200	0·200	0·003
0·280	0·282	0·002
0·320	0·317	0·002
0·400	0·394	0·006

Effect of light

The absorbance of the fully developed coloured products was measured at the usual time after development and after the solutions had been kept (*a*) in darkness for 1 month, (*b*) exposed to diffused daylight for 1 week, (*c*) exposed to direct sunlight for 2 hr. No absorbance changed by more than 2%. This is a considerable improvement on the Griess–Ilosvay reaction.[12]

Interferences

The following ions do not interfere, when present in 1000-fold molar excess over nitrite (0·66 ppm): ammonium, barium, calcium, iron(III), lead, lithium, magnesium, manganese(II), mercury(II), nickel, potassium, sodium, strontium, zinc, acetate, benzoate, borate, citrate, cyanide, fluoride, formate, lactate, molybdate, nitrate, oxalate, perchlorate, persulphate, phosphate, pyrophosphate, salicylate, sulphate, silicate, tartrate, trichloracetate, and thiocyanate.

The presence of aliphatic amines, strong reducing and strong oxidizing agents in nitrite samples is unlikely because of chemical incompatibility. Chlorine and nitrogen trichloride exclude the presence of nitrite, but they will be determined as nitrite by the Griess–Ilosvay reaction. In the proposed method they give rise to a different colour; equal volumes of sample and the mixed reagent develop a greenish yellow colour, which turns green on addition of acid, indicating the presence of chlorine. In the presence of copper the results are low. Vanadate brings about a colour change.

Interference by coloured substances may usually be avoided by using as a blank a mixture of the coloured sample solution with ethanolic citric acid solution instead of the mixed reagent.

Applicability and comparison with other methods

The reagent mixture is applicable for detection of traces of nitrites. The high sensitivity and the specific nature of the reagent make it suitable for qualitative analysis also. The sensitivity and range of applicability of the methods proposed are compared with other procedures, in Table III.

TABLE III.—COMPARISON OF METHODS

Reagents	Molar absorptivity $\times 10^{-3}$	Determination limit,* $\mu g\ NO_2^-$	Average deviation, %	Time needed, *min*	Colour stability	Beer's law range, $\mu g\ NO_2^-$	Ref.
p-Nitroaniline and diphenylamine	50	0·98	Not stated	4	5 min	1–24	8
Sulphanilic acid and *N*-(1-naphthyl)-ethylenediamine	46	2·5	Not stated	16	16 hr	2·5–60	8,9
Sulphanilamide and *N*-(naphthyl)-ethylenediamine	40	5·8	Not stated	34	1 hr	5·8–65	8,10
Sulphanilamide and *N*-(naphthyl)-ethylenediamine	47	0·95	Not stated	10	1 hr	0·6–12	6,11
Sulphanilic acid and 1-naphthylamine	33			16	1 hr	1·4–35	8,9
Sulphanilic acid and 1-naphthylamine	46	1	Not stated	16	1 hr	0·6–5·8	5
p-Diaminodiphenylsulphone and diphenylamine							
At pH 1·8	15	3	1	60	2 hr	3–75	This work
At pH 0·1	55	1	2	360	2 hr	0·7–15	This work
At pH 0·1 with heating	44	1·2	2	45	2 hr	0·7–15	This work

* To give an absorbance of 0·1 in a 1-cm cell.

Zusammenfassung—Diaminodiphenylsulfon-Diphenylamin wird bei einer neuen kolorimetrischen Methode zur Bestimmung von Nitrit im Bereich von 0,1–2,5 mg/l bei pH 1,8 und 0,22–0,4 mg/l bei einem pH von etwa 0,1 eingesetzt. Die gefärbten Lösungen sind stabil, befolgen das Beersche Gesetz und sind zum Spurennachweis durch visuellen Vergleich geeignet. Die Methode ist selektiv: weder Chlor noch Stickstofftrichlorid geben ähnliche Farbreaktionen.

Résumé—On utilise la diaminodiphénylsulfonènediphénylamine dans une nouvelle méthode colorimétrique pour le dosage du nitrite dans des domaines de 0,1–2,5 mg/l à pH 1,8 et de 0,22–0,4 mg/l à pH environ 0,1. Les solutions colorées sont stables, suivent la loi de Beer et conviennent au dosage de traces par comparaison visuelle. La méthode est sélective et ni le chlore ni le trichlorure d'azote ne donnent de réactions colorées semblables.

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LOCATION AND ANALYSIS OF 2-DEOXY SUGARS ON CHROMATOGRAMS AND PHEROGRAMS BY FLUORESCENCE

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Summary—A group of new reagents for the location of 2-deoxy sugars is introduced. A representative reagent is 4′-aminoacetophenone, which gives a green trimethine fluorogen with at least 0·5 μg of 2-deoxyribose, 2-deoxygalactose, or 2-deoxyglucose under neutral or slightly acidic conditions and the orange fluorescent anion under alkaline conditions at a lower limit of ~5 μg. Reagents such as 2-thiobarbituric acid, aniline–diphenylamine, and 2,4-pentanedione give vivid fluorescent colours with these sugars. Aniline–diphenylamine reagent was a useful fluorescent agent for locating the purine nucleosides and nucleotides and DNA. A new attachment for the spectrophotofluorimeter has been evaluated. With this attachment fluorescence excitation and emission spectra are obtained directly from paper, glass fibre, or thin-layer chromatograms and pherograms in sizes up to 20 × 20 cm. Glass plates are handled as readily as paper chromatograms. The fluorescence spectra of the various fluorogens produced after separation were readily obtained directly from the chromatogram or pherogram. 2-Thiobarbituric acid and 4′-aminoacetophenone offered the greatest potential for future application to characterization and assay of 2-deoxy sugars. The aniline–diphenylamine procedure was the most useful for analysis of purine nucleosides and nucleotides and DNA. These various reagents show potential for application to air pollution studies in terms of location, characterization and assay of 2-deoxy sugars and their derivatives.

STRONG evidence has been obtained that a large proportion of the organic airborne particulates consists of polyhydroxy organic compounds. These are mainly furfural precursors[1] and α-glycollic derivatives[2] of various types. More selective and sensitive characterization of these compounds would require separation, location and fluorimetric examination. Many separation methods for these compounds are available in the literature; however, since the compounds are neither coloured nor fluorescent, location methods are required.

Among the polyhydroxy compounds the 2-deoxy sugars are of special importance, mainly because 2-deoxy-D-ribose with phosphoric acid makes up the backbone of DNA, the genetic material of all life forms. Pre-viral, viral and viral-breakdown materials could be expected to be an important source of atmospheric DNA and its possible decomposition products. These sugars have been determined colorimetrically with diphenylamine,[3] 3,5-diaminobenzoic acid,[4] tryptophan,[5] xanthydrol,[6] thiobarbituric acid,[7] and MBTH.[2]

The available methods for locating 2-deoxy sugars on paper chromatograms mainly consist of direct reaction with a reagent or oxidation with periodic acid followed by reaction with an appropriate reagent. Examples of the first type are reaction of the sugar with a methanolic solution of boric and hydrochloric acids to give greyish-blue spots with purple fluorescence,[8] or reaction with vanillin.[9] The oxidative methods consist of oxidation of the 2-deoxy sugar to malonaldehyde followed by reaction with nitroprusside and piperazine, thiobarbituric acid,[10,11] or *p*-nitroaniline.[12]

In this paper various methods for the location and characterization of 2-deoxy sugars are introduced, compared with literature methods, and investigated for fluorimetric use.

EXPERIMENTAL*

Reagents

The various carbohydrates, in purest form, were obtained from commercial sources. *p*-Nitroaniline, 4′-aminoacetophenone, 4,4′-diaminodiphenylsulphone, ethyl *p*-aminobenzoate, thiobarbituric acid and diphenylamine were obtained commercially, and before use were recrystallized until they gave a constant melting point. Aniline was distilled over zinc before use. 2,4-Pentanedione was used as obtained.

*Apparatus**

An Aminco-Bowman spectrophotofluorimeter equipped with a solid sample accessory was used with the following settings: sensitivity 50, phototube RCA type 1P21, and an appropriate slit arrangement for reasonable sensitivity and resolution. Pretreatment of chromatograms before direct spectrophotofluorimetry has been discussed.[13] Pherograms were examined in the same fashion as chromatograms.

With the solid sample accessory the chromatogram or pherogram must be cut into small pieces before fluorimetric examination is possible. For this work the Aminco motorized thin-film scanner was modified with a prototype attachment (available from Aminco) that eliminates the glass fibre optics. With this modification, fluorescence excitation and emission spectra in the ultraviolet and visible regions can be obtained directly from the chromatogram or pherogram. Plates as large as 20 × 20 cm can be used. In the scanner equipped with glass fibre optics, light passes through the chromatogram or pherogram and through the glass fibres. Consequently, any fluorescence of these parts becomes background or blank fluorescence. With the prototype attachment quartz optics are used and light reflected off the chromatogram or pherogram does not come into contact with glass. Thus, a fluorescence spectrum with much less background interference is obtained, and any fluorescent spot separated on a chromatogram or a pherogram can be scanned at appropriate excitation and emission wavelengths.

Fluorimetric examination of chromatogram or pherogram

A piece of glass, plastic, or paper approximately 1 cm square is cut out of the chromatogram or pherogram. The adsorbent face is covered with a piece of black plastic (1 × 5 cm) containing a slit 2·5 mm square through which the spot is illuminated by the excitation light. This assembly is fastened with a piece of tape. The dry spot is fumed with trifluoroacetic acid fumes. The assembly is placed in the sample compartment with the uncovered spot perpendicular to and facing the light beam from the excitation monochromator. The excitation and emission spectra are obtained. A blank run is made on an uncontaminated area (of the pherogram or chromatogram) with the same R_f value as standard or unknown.

With the scanner containing the prototype attachment, fluorescent spots on a 20 × 20 cm plate can be readily examined so as to obtain their emission spectra.

Spray solutions

Periodate. Aqueous sodium periodate, 0·02*M*.

Periodic acid–γ-collidine. Periodic acid (0·67 g) and γ-collidine (2 ml) dissolved in methanol (98 ml).

4′-Aminoacetophenone. Alcohol (1%)–concentrated hydrochloric acid solution (4:1, v/v). Other amine spray solutions that were used were of similar composition, the amines used including

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* Mention of commercial products does not constitute endorsement by the Public Health Service.

4,4′-diaminodiphenylsulphide, 4,4′-diaminodiphenylsulphone, ethyl *p*-aminobenzoate, and *p*-nitroaniline.

Aniline–diphenylamine. Ten volumes of a solution of 1 ml of aniline and 1 g of diphenylamine in 100 ml of acetone were mixed with 1 volume of 85% phosphoric acid.

2,4-*Pentanedione.* Ammonium acetate (15 g), 2,4-pentanedione (1 ml) and glacial acetic acid (0·3 ml) diluted to 100 ml with methanol.

Dip solutions

Periodic acid. Aqueous H_5IO_6 solution (2·28%)–acetone (1:20 v/v). Mix immediately before use.

Alkaline solutions. A 10% solution of 1*M* methanolic tetra-n-butylammonium hydroxide in dimethylformamide. Mix before use.

4′-*Aminoacetophenone.* A 1% solution in 95% ethanol containing 1 ml of concentrated hydrochloric acid and 0·056 ml of ethylene glycol. Other amine dip solutions that were used were of similar composition, the amines used being 4,4′-diaminodiphenylsulphone, ethyl *p*-aminobenzoate, and *p*-nitroaniline.

2-*Thiobarbituric acid.* Dissolve 1 g of thiobarbituric acid and 0·056 ml of ethylene glycol in boiling ethanol and dilute to 100 ml with ethanol.

Periodate–aromatic amine spray procedure

Spray with periodate solution. After 6 min spray with the aromatic amine solution. Read the fluorescence colour under ultraviolet light and obtain the fluorescence spectra directly from the paper.

Periodate–aromatic amine or thiobarbituric acid dip procedure

Dip in periodic acid solution. Dry and dip into the aromatic amine or thiobarbituric acid (TBA) solution. Dry and heat at 60° for 1 min with the aromatic amine and for 15 min with TBA. Read visible colour and fluorescence. Scan or run fluorescence spectra immediately.

Alternatively, after the heating step of the aromatic amine reaction, dip into the tetrabutylammonium hydroxide solution. Read colour and fluorescence. Determine fluorescence excitation and emission spectra of spot, or elute with a small volume of the alkaline solution and from its absorption or fluorescence spectrum assay for the deoxy sugar derivative.

Aniline–diphenylamine spray procedure

Spray the chromatogram or pherogram with the aniline–diphenylamine reagent. Heat at 80–90° in an oven for 4 min. With longer heating the cellulose plate is discoloured. Read the fluorescence colours or scan fluorimetrically for estimation.

2,4-*Pentanedione procedure*

Spray the chromatogram or pherogram with the periodic acid–collidine solution. Wait 10 min. Spray with the pentanedione solution. Wait 10 min. Heat at 95° for 5 min. Read fluorescence colours.

DISCUSSION

Mechanism

The reaction of malonaldehyde with aromatic amines has been investigated previously.[14] The oxidation of 2-deoxyribose to malonaldehyde has been investigated.[7] The final fluorogens obtained through the reaction of the aromatic amine reagents with 2-deoxyribose or malonaldehyde exhibit closely similar spectral properties. Consequently, the reactions involved in the analysis of 2-deoxy-D-ribose are believed to take place as shown in Fig. 1.

2-*Deoxy sugars and derivatives*

In the sodium periodate spraying methods, yellow–green to green fluorescent colours at limits of 0·3–1 μg/cm² were obtained in most cases for 2-deoxyribose, 2-deoxy-galactose, 2-deoxyglucose, and deoxyinosine with 4′-aminoacetophenone, 4-nitroaniline, 4,4′-diaminodiphenylsulphone, and ethyl *p*-aminobenzoate on paper or on cellulose thin-layer plates. The compounds could also be located on silica gel plates with slightly higher detection limits except with *p*-nitroaniline, which gave negative results at 10 μg/cm^2.

A group of reagents were investigated for possible use in the fluorescent location and analysis of 2-deoxy sugars and their derivatives, Table I. The aromatic amine reagents produced brilliant green fluorescent colours with 2-deoxyribose, 2-deoxygalactose, and 2-deoxyglucose. *p*-Nitroaniline gave a blue–green non-fluorescent colour with the 2-deoxy sugars after alkaline treatment. The other aromatic amines gave orange to yellow fluorescent colours with the deoxy sugars after treatment with alkali. These fluorescent colours in alkaline solution were much less stable than the neutral fluorescent colours. On a chromatogram or pherogram they were much less stable than in solution. Part of this lack of stability is due to the ready elution of the final fluorogen by the alkaline dip reagent. This disadvantageous elution should be useful, however, in assaying the material by colorimetry or fluorimetry following elution.

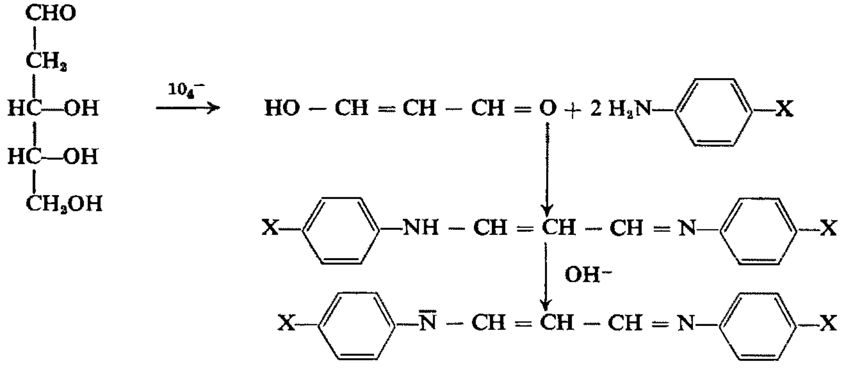

FIG. 1.—Reaction scheme determination of 2-deoxyribose with 4′-aminoacetophenone.

Many types of 2-deoxyribose derivatives gave negative results in the aromatic amine procedures. With a few of these reagents deoxyinosine gave positive results. With the amine reagents and the 2,4-pentanedione and 2-thiobarbituric acid reagents it is necessary to hydrolyse the derivatives to form free 2-deoxyribose before these reagents can be used successfully in the analysis of the derivatives.

The aniline–diphenylamine reagent gave fluorescent colours with the 2-deoxy sugars and the purine nucleosides. The pyrimidine derivatives, such as deoxycytidine, deoxycytidylic acid, thymidine, and thymidylic acid gave negative results. These latter compounds are more difficult to hydrolyse to 2-deoxyribose than are the purine derivatives. Thus, the two types of derivatives can be differentiated.

With 2-thiobarbituric acid the 2-deoxy sugars gave a red spot with yellow fluorescence. To the eye the visible and fluorescent colours of this spot were stable for weeks. The background changed little with time, unlike the background colour obtained with 4′-aminoacetophenone, which darkened in a few hours.

2-*Deoxy-D-ribose*. Many methods have been used for the location and assay of 2-deoxyribose. Methods introduced in this paper are compared in Table II with the thiobarbituric acid, aniline–diphenylamine, and 2,4-pentanedione procedures. Among these various methods the two that use 4′-aminoacetophenone and TBA

TABLE I.—LOCATION AND FLUORESCENCE COLOURS* OF 2-DEOXY SUGARS AND THEIR DERIVATIVES ON PAPER CHROMATOGRAMS AND PHEROGRAMS

Compound	Determination limit, μg and colour of fluorescence*										
	R†Ac		R†NO$_2$		R†$_2$SO$_2$		R†COOEt			$C_6H_5NH_2$	2,4-Pentanedione
	Neutral	Alk	Neutral	Alk	Neutral	Alk	Neutral	Alk	TBA‡	$(C_6H_5)_2NH$	
2-Deoxyribose	G(0·5)	O(5)	G(2)	BGc(3)	G(0·7)	Y(4)	G(0·4)	O(2)	Y(0·7)	Y(1)	YG(5)
2-Deoxygalactose	G(0·7	O(7)	G(3)	BGc(3)	G(5)	Y(5)	G(0·8)	O(5)	Y(0·9)	WBr(0·5)	YG(3)
2-Deoxyglucose	G(0·5)	O(5)	G(3)	BGc(3)	G(4)	Y(4)	G(0·8	O(5)	Y(0·7)	WBr(0·5)	YG(3)
Deoxyadenosine										Y(5)	
Deoxyadenosine-5′-phosphate										Y(0·7)	
Deoxycytidine											
Deoxycytidylic acid											
Deoxyguanosine										Y(0·7)	
Deoxyguanosine-5′-phosphate										Y(0·7)	
Deoxyinosine					G(7)		G(8)		Y(7)	Y(0·7)	
DNA										1Y(6)	
5-Hydroxymethylfurfural	G(0·5)						G(0·8)		Yc(0·9)		
Thymidine											
Thymidylic acid											

* B = blue, Br = brown, G = green, O = orange, R = red, W = white, Y = yellow. Yc signifies a yellow visible colour with no fluorescence.
† R = p—$H_2NC_6H_4$.
‡ Fluorescent spots gave a pink colour with the same detection limit.

TABLE II.—LOCATION AND FLUORESCENCE COLOURS OF 2-DEOXYRIBOSE ON VARIOUS MEDIA

Adsorbent	Fluorescence colour* and determination limit, μg										
	R†Ac		R†NO$_2$		R†$_2$SO$_2$		R†COOEt			$C_6H_5NH_2$	
	Neutral	Alk	Neutral	Alk	Neutral	Alk	Neutral	Alk	TBA‡	$(C_6H_5)_2NH$	2,4′-Pentanedione
Paper	G(0·5)	O(5)	G(2)¶	BGc(3)	G(0·7	Y(4)	G(0·4	O(2)	Y(0·7)	Y(1)**	YG(5)
GFP-Silica Gel			Yc(20)	BGc(3)	Yc(15)		G(7)	O(7)	Y(7)	Y(6)	
TLC-Silica Gel	G(0·3)	O(3)	Yc(15)	Gc(2)	Yc(2)	Y(15)	G(2)	O(5)	Y(4)	Y(2)	Y(15)
TLC-Cellulose	G(0·3	O(4)	G(3)	BGc(3)	G(0·9)	Y(0·9)	G(0·7)	YO(0·7)	Y(1·3)		

* Colour definitions as in Table I.
† R = p—$H_2NC_6H_4$.
‡ Also pink colour at same detection limit.
¶ On paper F 455/505.
** On paper F 455, 470/525.

reagents appear to offer the greatest potential for further development and application. These two reagents gave the most vivid fluorescent colours. The 4′-aminoacetophenone procedure was the most sensitive. Another advantage of this procedure was that the colour of the 2-deoxy sugar spot became visible even before heat was applied.

The types of fluorescence spectra obtained in the analysis of 2-deoxyribose with 4′-aminoacetophenone and 2-thiobarbituric acid on paper chromatograms are shown in Fig. 2.

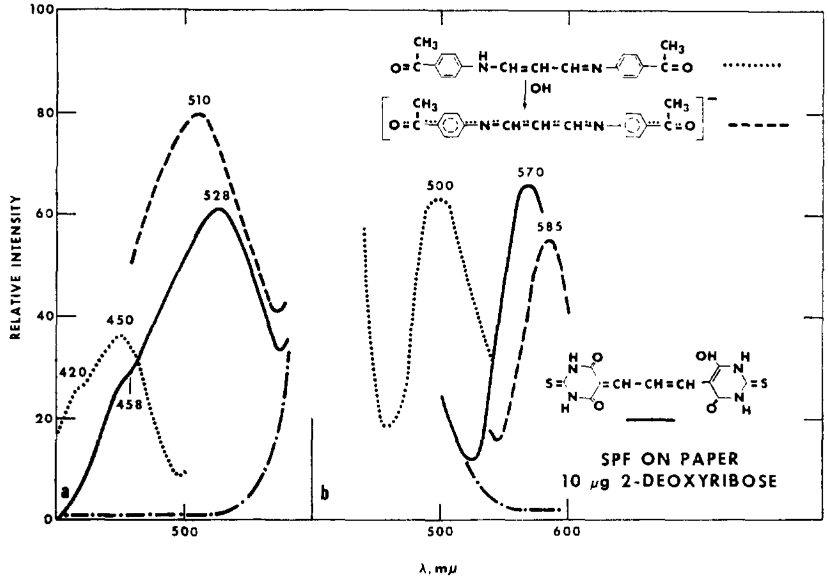

FIG. 2.—Fluorescence excitation (*a*) and emission (*b*) spectra of fluorogens obtained in the determination of 10 μg of 2-deoxyribose. (——) Thiobarbituric acid procedure, F 458/600 at meter multiplier (MM) 0·01 and 1P21 phototube. (. . .) 4′-Aminoacetophenone dip procedure, neutral spectra at F 400/550 and MM = 0·01 and 1P21 phototube. (– – –) 4′-Aminoacetophenone dip procedure, alkaline spectra at F 460/600 and MM 0·001 and R 136 phototube. Fluorescence fades within a few minutes.

CONCLUSIONS

Preliminary results indicate that the aromatic amine reagents can be used for the assay of 2-deoxyribose and other 2-deoxy sugars and other types of malonaldehyde precursors. If necessary, the final chromogen or fluorogen can be readily eluted by dimethylformamide and then assayed. In addition, with the new scanning attachment it should be possible to do a direct colorimetric or fluorimetric assay of the 2-deoxy sugars separated on a chromatogram or a pherogram, following treatment with one of the aromatic amines or TBA.

Another possibility to be explored before the procedures can be applied to air pollution studies is the preliminary hydrolysis of nucleosides, nucleotides, and deoxyribose nucleic acid to products that can be analysed by these procedures.

Zusammenfassung—Es wird eine neue Gruppe von Reagentien zur Sichtbarmachung von 2-Desoxyzuckern eingeführt. Ein Beispiel ist 4′-Aminoacetophenon, das mit wenigstens 0,5 μg 2-Desoxyribose, 2-Desoxygalactose oder 2-Desoxyglucose in neutralem oder schwach saurem Medium ein grünes Trimethin-Fluorogen liefert, in alkalischem

Medium bei einer unteren Grenze von etwa 5 μg das orange fluoreszierende Anion. Reagentien wie 2-Thiobarbitursäure, Anilin-Diphenylamin und 2,4-Pentandion geben lebhafte Fluoreszenzfarben mit diesen Zukern. Anilin-Diphenylamin war ein nützliches Agens zur Lokalisierung der Purin-Nucleoside und Nucleotide sowie von DNS. Ein neuer Zusatz zum Spektrophotofluorimeter wurde entwickelt. Mit diesem Zusatz erhält man direkt von Papier-, Glasfaser- oder Dünnschichtchromatogrammen oder Pherogrammen in Größen bis 20 × 20 cm Fluoreszenzanregungs- und -emissionsspektren. Glasplatten lassen sich ebenso leicht handhaben wie Papierchromatogramme. Die Fluoreszenzspektren der verschiedenen nach Trennung erzeugten Fluorogene ließen sich leicht direkt vom Chromatogramm oder Pherogramm abnehmen. 2-Thiobarbitursäure und 4′-Aminoacetophenon boten den größten Anwendungsbereich zu Charakterisierung und Nachweis von 2-Desoxyzuckern. Das Verfahren mit Anilin-Diphenylamin war am nützlichsten bei der Analyse von Purin-Nucleosiden, Nucleotiden und DNS. Die Reagentien versprechen Nutzen bei der Anwendung auf Untersuchungen der Luftverunreinigung durch Lokalisierung, Charakterisierung und Nachweis von 2-Desoxyzuckern und ihren Derivaten.

Résumé—On présente un groupe de nouveaux réactifs pour la localisation des 2-déoxy sucres. Un réactif type est la 4′-aminoacétophénone, qui donne un fluorogène triméthine vert avec au moins 0,5 μg de 2-déoxyribose, 2-déoxygalactose ou 2-déoxyglucose dans des conditions neutres ou légèrement acides, et l'anion fluorescent orangé dans des conditions alcalines avec une limite inférieure d'environ 5 μg. Des réactifs tels que l'acide 2-thiobarbiturique, l'aniline-diphénylamine et la 2,4-pentanedione donnent des couleurs fluorescentes vives avec ces sucres. Le réactif anilineàdiphénylamine est un agent utile pour la localisation des nucléosides et nucléotides puriques et de l'ADN. On a estimé la valeur d'un nouveau dispositif pour le spectrofluorimétre. Avec ce dispositif, on obtient les spectres d'excitation et d'émission de fluorescence directement à partir de chromatogrammes sur papier, fibre de verre ou en couche mince et de phérogrammes, de dimensions allant jusqu'à 20 × 20 cm. Les plaques de verre sont traitées aussi aisément que les chromatogrammes sur papier. Les spectres de fluorescence des divers fluorogénes produits aprés séparation ont été aisément obtenus directement du chromatogramme ou pherogramme. L'acide 2-thiobarbiturique et la 4′-aminoacétophénone offrent les plus grandes possibilités pour l'application future à la caractérisation et à la détermination des 2-déoxy sucres. La technique à l'aniline–diphénylamine est la plus utile pour l'analyse des nucléosides et nucléotides puriques et de l'ADN. Ces divers réactifs montrent des possibilités d'application aux études sur la pollution de l'air pour ce qui est de la localisation, de la caractérisation et de la détermination des 2-déoxy sucres et de leures dérivés.

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STUDIES WITH DITHIZONE—XII*

FORMATION OF THIADIAZOLINES BY CONDENSATION WITH ALDEHYDES AND KETONES

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Summary—The red colour that develops when mineral acids are added to solutions of dithizone (I; 3-mercapto-1,5-diphenylformazan) in certain samples of dioxan is mainly due to the formation of 2-methyl-3-phenyl-5-phenylazo-1,3,4-thiadiazoline (II) derived in part from adventitious traces of 2-methyldioxalane. A purple compound of molecular formula $C_{13}H_{10}N_4S$ is also formed from (I) by an independent and slower reaction. The thiadiazoline (II) is readily prepared from (I) and acetaldehyde, but analogous compounds from formaldehyde benzaldehyde, acetone and ethyl methyl ketone are obtained in better yield by starting from diphenylthiocarbazide. Di-*p*-tolyldithizone gives similar reactions. Reduction of the thiadiazoline (II) [which has spectra very closely resembling those of 1:1 complexes of (I) with arylmercury (II) cations] with ammonium hydrogen sulphide in ethanol yields diphenylthiocarbazide by opening of the hetero-ring and elimination of an alkyl residue from the intermediate 3-alkylmercapto-1,5-diphenylformazan. Other examples of nucleophilic displacements from the formazan group by SH^- have been investigated.

DURING an extensive investigation of the acid dissociation constant of dithizone (3-mercapto-1,5-diphenylformazan, H_2Dz; I, $R^1 = H$, Ar = Ph) and its analogues, absorptiometric measurements of relative concentrations of the strongly coloured species H_2Dz and HDz^- were carried out on a series of buffer solutions made up in various dioxan–water mixtures. Previous experience with these reagents had led us to expect that decomposition would become increasingly troublesome as the medium became more alkaline,[1] and in similar measurements in 50% aqueous dioxan Freiser *et al.*[2,3] found it necessary to extrapolate their absorbance measurements to zero time. In our hands, however, little difficulty was experienced when measurements in the more alkaline solutions were conducted under anaerobic conditions with very pure reagents. On the other hand, solutions in the more acidic buffers ($[H^+] \geqslant 0{\cdot}1M$) sometimes unexpectedly changed colour from green to red in the course of a few minutes.

This colour change is illustrated in Fig. 1 for a solution of di-*p*-tolyldithizone (I; $R^1 = H$, Ar = *p*-tolyl) in 70% (v/v) dioxan–water containing sufficient hydrochloric acid to give a $1{\cdot}0M$ solution. Similar results were found with dithizone itself and with di-*p*-anisylthiocarbazone (I; $R^1 = H$, Ar = *p*-methyoxyphenyl). Although the rate of reaction decreased when the acidity was reduced to $0{\cdot}5M$, the nature of the mineral acid used appeared to be unimportant; similar changes occurred with

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* Part XI—H. Irving and A. M. Kiwan, *J. Chem. Soc.*, 1963, 4288.

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perchloric and sulphuric acids. There was no obvious change in behaviour when the dioxan content was progressively reduced to 30%, but 70% dioxan was used in all the subsequent work in view of its greater solvent powers.

The clearly defined isosbestic points (Fig. 1) at 467 and 549 mμ (or at 458 and 537 mμ for dithizone itself and at 458 and 576 mμ for its *p*-methoxy analogue) immediately suggested an equilibrium between the thiocarbazone (λ_{max} 450 and 620 mμ) and some protonated species with λ_{max} 500 mμ; if no side-reactions occur this species would have a high molar absorptivity of ∼20000. The slowness of the reaction raised doubts as to the correctness of this hypothesis, which was definitely disproved by the observation that the spectrum of a solution of $1\cdot214 \times 10^{-5}M$ di-*p*-tolyldithizone in 70% dioxan-water at $[H^+] = 1\cdot0M$ taken 70 min after mixing the components, and which had not changed after a further 70 min, was quite unaffected by the addition of an exact equivalent of alkali, remaining unchanged for at least 16 hr.

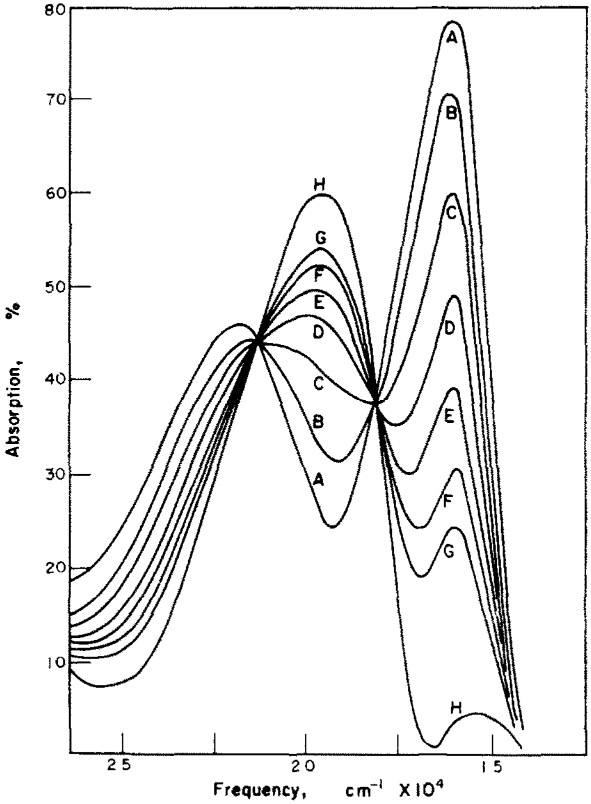


Fig. 1.—Spectra of $1\cdot776 \times 10^{-5}M$ di-*p*-tolyldithizone in 70% v/v dioxan-water containing hydrochloric acid ($[H^+] = 1\cdot0M$).
Curves *A* to *H* show the changes after 1·1, 5, 10, 15, 20, 25, 30 and 63 min respectively. After a further 27 min the spectrum coincided with that labelled *H*.

A freshly prepared solution of dithizone in glacial acetic acid is green with peaks at 440 and 625 mμ, but after several days the colour changes to purple, and though there is a broad band at ∼500 mμ (similar to the intense band at 532 mμ in the purple solutions of dithizone in conc. hydrochloric acid), this is subordinate to a much more intense band at 312·5 mμ (Fig. 2). Clearly different species are involved in this reaction and the new species absorbing at 312·5 mμ arises from the "purple compound" (*A*) described below.

The possibility that the red colour of solutions of dithizone in acidified aqueous dioxan was due to oxidation by peroxides in the dioxan used was eliminated by

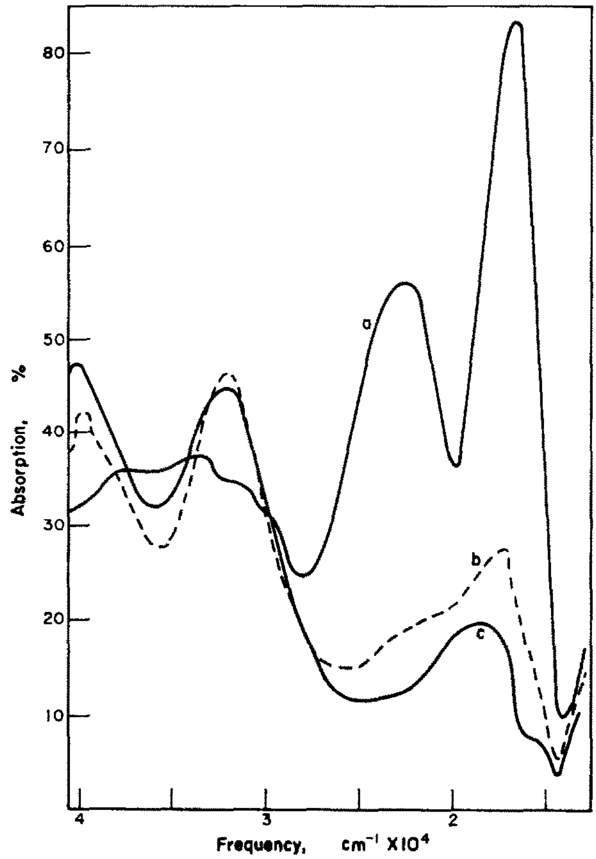


Fig. 2.—Spectrum of 2·47 × $10^{-5}M$ dithizone in redistilled glacial acetic acid. (*a*) Immediately after preparation; (*b*) (broken line) after 4 days; (*c*) after 7 days.

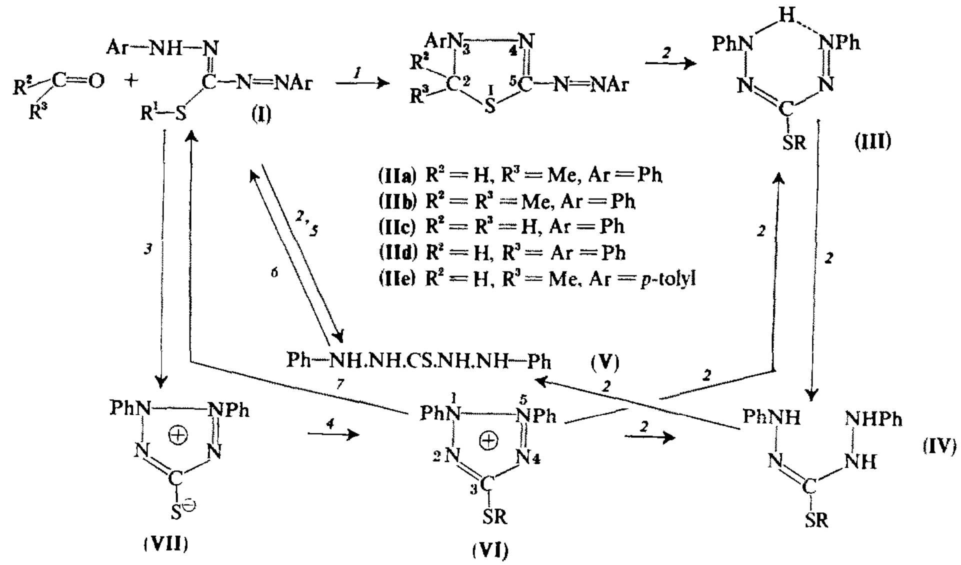
deliberately adding hydrogen peroxide. The peak at 620 mμ due to dithizone then disappeared during some 40 min while the dithizone peak at 450 mμ also decreased in intensity and underwent a hypsochromic shift. No peak appeared at ~500 mμ and the spectrum of the final solution closely resembled that of the "yellow oxidation product" referred to by many workers.[4] The solution was shown to contain anhydro-5-mercapto-2,3,diphenyltetrazolium hydroxide (VII) together with a smaller amount of a substance that regenerated dithizone on standing with an aqueous solution of sodium thiosulphate.

Dioxan appeared to be essential to the formation of the substance absorbing at 500 mμ; solutions of dithizone in ethanolic 1·0*M* perchloric acid or in 0·16*M* sulphuric acid in 70% glacial acetic acid–water mixture decomposed in a few hours and gave no new substances absorbing in the visible region. Isolation of the substance absorbing at 500 mμ was attempted by carrying out the reaction with 1-g quantities of dithizone, but the reaction mixture was then shown chromatographically to contain two products, (*A*) a purple crystalline compound with a coppery lustre, m.p. 180–2° (decomp.), and (*B*) a more soluble dark red crystalline compound m.p. 99° (decomp.) which dissolved in most organic solvents but not in water or aqueous alkali. When the time of reaction and the relative proportions of acid, dithizone and dioxan were varied systematically, the ratio of the amounts of purple compound and red product appeared to increase with time. That the red compound was a precursor of the purple compound was disproved by a variety of experiments, and the correct explanation is that there is an initial rapid reaction between dithizone and aldehydic impurities liberated by the action of acid on the dioxan–water mixture, and when all these have been consumed the relatively slow reaction between the excess of dithizone and the acid then leads to increasing amounts of compound *A*.

Compound *A*, of molecular formula $C_{13}H_{10}N_4S$, had a characteristic spectrum in ethanol (λ_{max} 314 and 536–538 mμ, ε_{max} 23·6 × 10^3 and 9·04 × 10^3) and was identified by mixed melting point and comparison of its absorption spectrum with that of a specimen of the "beautiful reddish-bronze crystalline compound" prepared by heating dithizone or "dehydrodithizone" with glacial acetic acid according to Ogilvie and Corwin's procedure,[5] and rigorously purified. Not all its reactions agreed with those reported by Ogilive and Corwin and its investigation will form the subject of a later paper.

The spectrum of compound *B* in 70% dioxan showed that this was responsible for the colour changes observed in an acidic solution of dithizone in this solvent. Its molecular formula, $C_{15}H_{14}N_4S$, (confirmed by vapour pressure osmometry in chloroform) differs from that of dithizone, $C_{13}H_{12}N_4S$, by an additional two carbon and two hydrogen atoms which must clearly have been derived from the solvent. Gas chromatography of the dioxan used, which had been purified by Freiser's method[2,3] revealed the presence of an impurity which was absent from dioxan purified according to Weissburger and Proskauer's method,[6] but present to the extent of about 1% in an untreated commercial sample of dioxan. This impurity was shown by gas chromatography to be 2-methyldioxalane. This would have been eliminated in Weissburger and Proskauer's procedure which includes heating under reflux with hydrochloric acid to decompose acetals, followed by a stage to eliminate aldehydes. These steps are omitted in Freiser's procedure which is based on prolonged refluxing over metallic sodium followed by fractionation. Acid hydrolysis of the 2-methyldioxalane gives rise to acetaldehyde which condenses with dithizone (**I**; R^1 = H, Ar = Ph) to give 2-methyl-3-phenyl-5-phenylazo-1,3,4-thiadiazoline (**IIa**; R^2 = H, R^3 = Me, Ar = Ph). This was very readily synthesized by mixing dithizone with acetaldehyde and adding a few drops of conc. hydrochloric acid.

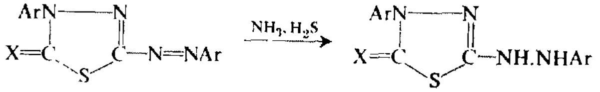
Condensation with acetone to give 2,2-dimethyl-3-phenyl-5-phenylazo-1,3,4-thiadiazoline (**IIb**; $R^2 = R^3$ = Me, Ar = Ph) proceeded similarly as did that with ethyl methyl ketone although the red product in this case was not obtained analytically pure. Similar condensations were carried out with di-*p*-tolylthiocarbazone (**I**; R^1 = H, Ar = *p*-tolyl). Preund[7,8] has reported that diphenylthiocarbazide (**V**) condenses with phosgene or thiophosgene to give the same products (**VIII**; X = O or S) as those obtained from dithizone itself. Pel'kis *et al.*[9,10] have recently extended this method to the synthesis of a large number of homologues of **VIII** (X = S). Clearly



Reagents: *1*, HCl; *2*, NH_3 and H_2S in ethanol at 0°; *3*, $K_3Fe(CN)_6$ or NaOH–H_2O_2 when $R^1 = H$; *4*, (*a*) MeI for R = Me, (*b*) chloracetic acid for $R = -CH_2.CO_2H$; *5*, Zn–NaOH when $R^1 = H$; *6*, boiling NaOMe–MeOH; *7*, alkaline solution of dextrose.[5]

the loss of two hydrogen atoms must occur at some stage in this reaction and we now find that dithizone can be replaced with advantage by diphenylthiocarbazide (V) in condensations with carbonyl compounds. Thus formaldehyde and benzaldehyde gave rise to (IIc), ($R^2 = R^3 = H$, Ar = Ph) and (IId) (R^2 = Ar = Ph) respectively.

VIII



IX

The NMR spectrum of 2-methyl-3-phenyl-5-phenylazo-1,3,4-thiadiazoline (IIa) recorded in deuterochloroform at 60 Mc showed the symmetrical doublet due to CH_3 (centered on $\tau = 8{\cdot}4$), the 1:3:3:1 quartet due to CH (centered on $\tau = 3{\cdot}9$) and a complex group due to two sets of 5 equivalent protons; the integrated curves confirm the groupings of 3,1, and 10 protons respectively.

Preund *et al.*[7,8] have shown that the ketones or thioketones (VIII; X = O or S) are readily reduced to the corresponding hydrazo compounds (IX; X = O or S) when treated with an ethanolic solution of ammonium hydrogen sulphide. When, however, the red compound (IIa) was reduced under these conditions, the colourless product, obtained in over 90% yield proved unexpectedly to be diphenylthiocarbazide (V), identified by mixed m.p., infrared spectrum, and oxidation to dithizone.

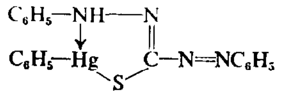
By contrast with the behaviour of the thiadiazolines (VIII) where the azo-grouping in the side chain is reduced to a hydrazo-group, the hetero-ring remaining untouched, reduction of (IIa) must have opened up the heterocyclic ring with the subsequent elimination of the alkyl residue $-CHR^2R^3$. Had the ring ruptured between C(2) and S(1) an *N*-alkyldithizone would have resulted, subsequent reductive de-alkylation of which would seem unlikely in view of the resistance of *N*-alkylanilines and phenylhydrazines to reduction by ammoniacal hydrogen sulphide at 0°. If, on the other hand, the heterocyclic ring is opened between N(3) and C(2) the primary intermediate would be an *S*-alkyldithizone (*e.g.*, **III**). Corwin and Olgivie[5] have already shown that the reduction of 3-methylmercapto-1,5-diphenyltetrazolium iodide (**VI**; R = Me) by ammonium hydrogen sulphide in ethanol at 0° gives rise first to *S*-methyldithizone (**III**; R = Me) which they were able to isolate, and then to an unstable white crystalline substance which was readily reoxidized to *S*-methyldithizone on exposure to the air. This substance, tentatively formulated as (**IV**) (R = Me), gave diphenylthiocarbazide (**V**) when allowed to stand in contact with ethanolic ammonium hydrogen sulphide for 4 hr. 3-Carboxymethylmercapto-1,5-diphenyltetrazolium iodide (**VI**; R = $-CH_2{\cdot}CO_2H$) underwent a similar reductive sequence[5] and we now find that the end-product of the reduction of (**VII**) is likewise diphenylthiocarbazide (**V**).

These processes which involve the elimination of an *S*-alkyl group must be due to the nucleophilic displacement of RS^- by the excess of HS^- added, followed by tautomeric rearrangement to the isomeric thioketone. The conversion of a 3-chloroformazan to the corresponding dithizone is a further example of this process[11,12] and in Bamberger's synthesis of dithizones from 3-nitroformazans[13–15] it is postulated that the 3-amino group obtained intermediately by treatment with alcoholic ammonium hydrogen sulphide is subsequently displaced by SH^-.

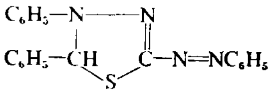
All the new thiadiazolines have very similar spectra (Fig. 3). The effect of the *p*-methyl substituent in (**IIe**) is to increase the intensity of the absorption and to produce a very small bathochromic shift of the main peak in the visible region (Table I). A point of considerable interest is the close similarity between the spectra of these new heterocyclics and the 1:1 complexes of dithizone with arylmercury(II) cations[16–18]. Most of these show bands at 200, 260–280, ~320 and 450–550 mμ; the last three bands have been identified in almost all metal dithizonates although the positions and intensities of the absorption maxima are influenced by the nature of the metal.[19] The X-ray crystallographic study of mercury(II) dithizonate has disclosed a very strong bond between sulphur and mercury together with a co-ordinate bond to mercury from one of the nitrogen atoms co-ordinated to a phenyl residue.[20] By analogy the structure of phenylmercury(II) dithizonate may be represented as (**X**) and the formal similarity to the 1.3,4-thiadiazoline ring is immediately obvious.

TABLE I.—ULTRAVIOLET AND VISIBLE SPECTRA OF 1,3,4-THIADIAZOLINES WITH THAT OF PHENYLMERCURIC DITHIZONATE FOR COMPARISON

Compound	λ_{max} (ε_{max})			
(**IIa**)	206–7	266·5 (13·8 × 10^3)	shoulder ~300	492 (28·6 × 10^3)
(**IIb**)	206–7	plateau	305 (10·7 × 10^3)	460 (21·7 × 10^3)
(**IIc**)	206–7	266 (12·3 × 10^3)	shoulder	496 (29·3 × 10^3)
(**IId**)	206–7	265 (13·0 × 10^3)	310 (11·2 × 10^3)	493 (29·0 × 10^3)
(**IIe**)	206–7	268 (13·6 × 10^3)	shoulder	498 (33·3 × 10^3)
Phenylmercury dithizonate	204–5 (46·6 × 10^3)	263 (20·7 × 10^3)	322 (13·3 × 10^3)	476 (32·5 × 10^3)



(X)



(IId)

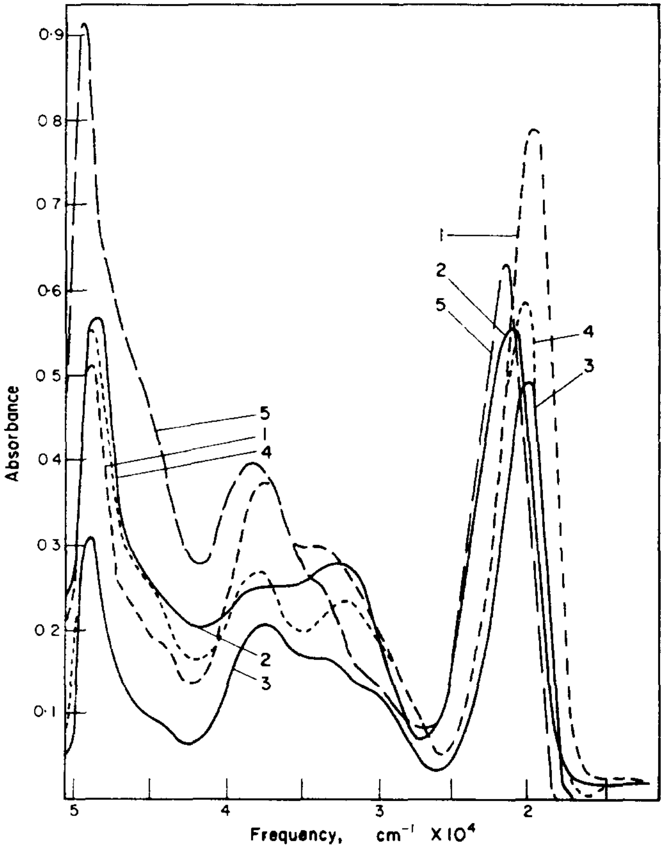


FIG. 3.—Ultraviolet and visible spectra of 1,3,4-thiadiazolines in ethanol. *1*—Substance IIa (the red compound *B*), 2·97 × $10^{-5}M$; *2*—substance IIb, 2·63 × $10^{-5}M$; *3*—substance IIc, 1·75 × $10^{-5}M$; *4*—substance IId, 2·06 × $10^{-5}M$; *5*—phenylmercury(II) dithizonate, 2·43 × $10^{-5}M$ in 75% v/v ethanol–water.

Duncan and Thomas[21] ascribe a band at 3139 cm^{-1} in the infrared spectrum of dithizone in carbon tetrachloride solution to the N—H stretching frequency and all metal dithizonates are said to show this vibrational feature in the region 3100–3300 cm^{-1}. The spectrum of diphenylcarbazide (V) in a potassium bromide disc is now found to show four bands in this region, which could well be due to the NH groups in this molecule. On the other hand, the complete absence of any bands in this region in the spectra of the 1,3,4-thiadiazoles IIa–IIe is a clear indication that oxidative coupling must have taken place when they are formed by the condensation of a carbonyl compound with dithizone or diphenylthiocarbazide.

The spectra of all the thiadiazoles show a number of high intensity bands in the 3067–3030 cm^{-1} region, and these are probably due to aromatic $=CH$ stretching. The very sharp and intense band at 2967 cm^{-1} for **IIa** and **IIb** and centered at 2976 cm^{-1} for **IIe** can be ascribed to the assymetric stretch of the CH_3 group (lit. 2962 ± 10 cm^{-1}); it is, of course, absent in the spectra of **IIc** and **IId**. The weak bands at 2920 and 2857 cm^{-1} in **IIc** have been assigned to the asymmetric and symmetric C—H stretch of the CH_2 group (lit. 2926 and 2853 cm^{-1}). A tertiary $\equiv$C—H stretching frequency would be expected at 2890 × 10 cm^{-1}. No such band appears in the spectrum of the 2,2′-dimethyl compound **IIa** which shows no structure between 2924 and 1590 cm^{-1}; overlap with neighbouring bands would prevent its identification in the other cases.

When potassium bromide discs were used no bands were observed in the region 2000–1650 cm^{-1} but with concentrated solutions in hexachlorobutadiene all the compounds showed typical overtone patterns of substituted aromatics. The 2-phenyl derivative **IId** showed 12 well-resolved bands which differentiated it from the other compounds studied. The bands of high intensity at 1590 ± 3 and 1520 ± 7 cm^{-1} in the spectra of all the compounds and bands of variable intensity at 1495 ± 10 cm^{-1} appear to be C=C skeletal vibrations, but those at ~1450 cm^{-1} may overlap the bands due to the asymmetric —$C(CH_3)$ group deformation in certain cases. The sharp band at 1466 cm^{-1} in the spectrum of **IIc** has been assigned to the CH_2 group deformation. The sharp bands centered at 1380 and 1364 cm^{-1} in the spectrum of **IIb** are due to the —$C(CH_3)_2$ group deformation vibrations (lit. 1385–1380 and 1370–1365 cm^{-1}). The bands in the 1250–1100 cm^{-1} region are doubtless due to N—C_6H_5 vibrations: Meriwether *et al.*[22] have assigned bands in this region which are found in the spectra of all metal dithizonates. The characteristic pattern in the region 835–792 cm^{-1} for **IIe** is typical of 1,4 aromatic disubstitution (lit. 860–800 cm^{-1}). Other assignments and typical spectra are given in detail elsewhere.[23]

In view of the characteristic spectra and high intensity of absorption (ε_{max} = 20000–33000) of the new 1,3,4-thiadiazolines it was hoped that they could be exploited for the quantitative absorptiometric determination of aldehydes and ketones, but the reaction with dithizone or diphenylthiocarbazide was too slow unless the appropriate catalyst was used in homogeneous solution, and even then preliminary concentration of the carbonyl compound was necessary and yields were variable. The reactions discussed above do, however, emphasize one of the problems constantly to be borne in mind when carrying out solution work with low concentrations of reactants: at the $10^{-5}M$ reactant level as little as 0·1% of foreign material in the solvent (*e.g.*, dissolved oxygen, moisture, or in this case 2-methyldioxalane) may lead to disturbing and unexpected side-reactions.

The purple compound (*A*) may have the bis-azo structure Ph.N=N.CS.N=N.Ph; further work on its reactions and a structure determination by X-ray crystallography will be reported elsewhere.

EXPERIMENTAL

Reagents

Commercial dioxan was purified[2,3] by refluxing over metallic sodium for 12 hr followed by fractional distillation immediately before use. This procedure does not remove 2-methyldioxalane; another procedure[6] was used for this when necessary.

Demineralized water was used to prepare all dioxan–water mixtures, and isopiestic ammonia and hydrochloric acid.[24] Glacial acetic acid and all organic solvents were redistilled immediately before use. Analar samples of dithizone were purified by methods previously described[23] and the ratio of the absorbances at 620 and 450 mμ of carbon tetrachloride solutions of the reagent was used as an index of purity. A value of 1·68–1·70 was regarded as satisfactory.

Absorption spectra were measured with a Unicam SP 700 recording spectrophotometer or with an SP 500, with matched silica cells. Before use these cells and all glassware needed were rigorously freed from every trace of metallic contamination and from oxidizing matter.

2-*Methyl*-3-*phenyl*-5-*phenylazo*-1,3,4-*thiadiazoline* (IIa)

Concentrated hydrochloric acid (4–5 drops) was added to a paste of dithizone (1 g) and redistilled acetaldehyde (4·5 ml, excess) and the mixture was cooled in an ice-bath and triturated with a glass spatula for 10–15 min. Chloroform (100–150 ml) was then added and the solution was shaken with water in a separatory-funnel. The aqueous phase was rejected and the organic phase washed twice with water and then with dilute ammonia to remove unreacted dithizone: it was then dried over anhydrous sodium sulphate and the solvent was distilled off under reduced pressure. The product was recrystallized from methanol to give dark red needles, m.p. 99–100° decomp. Yield 44%. A poorer yield (20%) was obtained when the condensation of diphenylthiocarbazide (V; 2·6 g) with acetaldehyde (1 ml) in presence of conc. hydrochloric acid (0·2 ml) was carried out slowly (2 hr) in ethanol (50 ml). (Found: C, 63·8%; H, 5·2%; N, 19·8%; S, 11·5% m.w. (vapour pressure osmometry in chloroform) 289: $C_{15}H_{14}N_4S$ requires C, 63·8%, H, 5·0%; N, 19·9%; S, 11·3%; m.w., 283.)

2,2′-*Dimethyl*-3-*phenyl*-5-*phenylazo*-1,3,4-*thiadiazoline* (IIb)

Dithizone (1·0 g) in acetone (50 ml) containing conc. hydrochloric acid (1·0 ml) was shaken mechanically for 1·5 hr. After removal of the solvent in a stream of air the sticky residue was dissolved in chloroform and transferred to a separatory-funnel, washed with water (3 × 50 ml) and the solution dried over anhydrous sodium sulphate. Chromatography on alumina with benzene as the eluent gave ultimately dark reddish-orange crystals which after two recrystallizations from methanol had m.p. 77–78° decomp. Yield 47%. (Found: C, 64·7%; H, 5·4%; N, 19·1%: $C_{16}H_{16}N_4S$ requires C, 64·9%; H, 5·4%; N, 18·9%.)

3-*Phenyl*-5-*phenylazo*-1,3,4-*thiadiazoline* (IIc)

Concentrated hydrochloric acid (0·4 ml) and 36% w/v aqueous formalin (2 ml) were added to a suspension of diphenylthiocarbazide (V, 2·6 g) in ethanol (50 ml) and stirred mechanically for 3 hr. Dark red crystals separated (0·25 g) and a further amount (1·87 g) was obtained by removing the solvent in a stream of air. A chloroform solution of the total crude product was transferred to a column of alumina and chromatographed with benzene; dark red crystals (0·6 g) were obtained on evaporation. After two recrystallizations from benzene these had m.p. 164–5° decomp. Yield 23%. (Found: C, 62·5%; H, 4·7%; N, 21·0%: $C_{14}H_{12}N_4S$ requires C, 62·7%; H, 4·5%; N, 20·9%.)

2,3-*Diphenyl*-5-*phenylazo*-1,3,4-*thiadiazoline* (IId)

Diphenylthiocarbazide (V, 2·6 g), benzaldehyde (2 ml, excess), concentrated hydrochloric acid (0·5 ml) in ethanol (70 ml) were shaken mechanically for 2·5 hr. A dark red solid (0·25 g) which separated, together with the red residue left after evaporation of the solvent in a stream of air, was taken up in chloroform, filtered from an unidentified white substance (0·58 g, m.p. 278–280° decomp.), and treated with a solution of sodium bisulphite to remove excess of benzaldehyde. Chromatography on alumina with a 1% solution of methanol in benzene as the eluent gave a prominent red band from which the thiadiazoline was isolated as red crystals, m.p. 144–5° decomp. Yield 23%. (Found: C, 69·7%; H, 4·7%; N, 16·3%: $C_{20}H_{16}N_4S$ requires C, 69·5%; H, 4·7%; N, 16·3%.)

2-*Methyl*-3-*p*-*tolyl*-5-*p*-*tolylazo*-1,3,4-*thiadiazoline* (IIe)

This compound was prepared from acetaldehyde and di-*p*-tolylthiocarbazone as described for the phenyl analogue. After two recrystallizations from methanol the red crystalline product had m.p. 156–7° decomp. Yield 20%. (Found: C, 65·6%; H, 5·7%; N, 18·2%: $C_{17}H_{18}N_4S$ requires C, 65·8%; H, 5·9%; N, 18·1%.)

Isolation of the compounds A *and* B

In a typical experiment, dithizone (1 g) suspended in a mixture of redistilled commercial dioxan (70 ml), concentrated hydrochloric acid (10 ml) and distilled water (20 ml) was shaken mechanically for 16 hr and then poured into water (100 ml). The reddish-brown solution obtained on extraction with chloroform (50 ml) was washed repeatedly with water to free it from dioxan. After being dried over anhydrous sodium sulphate the chloroform was allowed to evaporate at room temperature and the red residue (0·6 g) was taken up in chloroform (15 ml) and chromatographed on a column of neutral alumina. The less strongly adsorbed reddish-orange band was eluted with 1% ethanol in benzene and on removal of the solvent gave substance *B*, (0·15 g). The slower moving dark purple band was eluted with chloroform and gave 0·35 g of substance *A*.

Substance *A* gave deep purple crystals with a coppery lustre, m.p. 180–182°, from aqueous ethanol. Found: C, 61·5%; H, 4·0%; N, 22·0%. m.w. by vapour pressure osometry in chloroform, 246: $C_{13}H_{10}N_4S$ requires C, 61·4%; H, 3·9%; N, 22·0%; m.w. 254·3). Substance *A* was identified with the "isomeric dehydrodithizone" described by Ogilvie and Corwin,[5] by comparison with authentic samples prepared by heating (*a*) dithizone or (*b*) the syndnone (VII) under reflux with glacial acetic acid. After purification by chromatography and recrystallization from aqueous ethanol all the samples had identical melting points and absorption spectra.

The purple compound *A* was also obtained by boiling diphenylthiocarbazide (V, 2 g) in glacial acetic acid (15 ml) under reflux. The initially colourless solution changed to dark green (5 min) and then to purplish red (30 min). The reaction mixture was cooled, poured over ice and extracted with chloroform; sticky purple crystals were obtained (0·95 g) on removing the solvent in a current of air. The crude material was triturated with a small volume of chloroform and filtered from a greyish white solid (0·29 g) which after two recrystallizations from boiling ethanol formed light straw-coloured crystals, m.p. 200–201° decomp. This substance was identified as β-phenylthiosemicarbazide by mixed m.p. and the identity of its infrared spectrum with that of an authentic specimen.[15b]

Investigation of the impurity in dioxan by gas-liquid chromatography

A 5-foot column packed with 10% dinonyl phthalate on Celite was used with a hydrogen flame detector. Chromatograms were taken of (*i*) commercial dioxan, (*ii*) dioxan purified by Freiser's method,[2,3] (*iii*) dioxan purified by Weissburger and Proskauer's method,[8] (*iv*) 2-methyl-1,3-dioxalane prepared according to Hibbert and Timm[26] and carefully fractionated, (*v*) purified commercial acetaldehyde diethylacetal (1,1′-diethoxyethane), and (*vi*) redistilled acetaldehyde. With a constant flow-rate of carrier gas the main peaks of *i*, *ii* and *iii* had retention times of 71·3, 74·7 and 78·1 sec respectively but samples *i* and *ii* had subsidiary peaks at 51·0 and 54·3 sec respectively, which were identified as due to 2-methyldioxalane (retention time 53 secs in *iv*). Samples *i*, *ii* and *iii* were shown to be free from 1,1′-diethoxyethane (retention time 67·6 sec) and acetaldehyde (20·9 sec). By comparison with chromatograms containing known amounts of pure dioxan (*iii*) and 2-methyldioxalane (*iv*) it was estimated that the commercial dioxan or a specimen purified by Freiser's method contained about 1% of 2-methyldioxalane.

Reduction of 2-*methyl*-3-*phenyl*-5-*phenylazo*-1,3,4-*thiadiazoline* (*IIa*) *with ammonium hydrogen sulphide in ethanol*

A suspension of the thiadiazoline (IIa; 0·56 g) in ethanol (25 ml) was cooled to 0° and saturated with ammonia gas (10 min). Hydrogen sulphide was then bubbled in (10 min) whereupon ammonium hydrogen sulphide separated as shining leaflets. No colour change occurred at first but after 1·5 hr at room temperature a yellow solution resulted which was poured slowly over cracked ice; diphenylthiocarbazide (V) then separated as shining colourless platelets (0·47 g) which were collected, washed first with water and then with alcohol, and dried in a vacuum desiccator. After recrystallization from ethanol, the substance when heated changed colour to light green at 145–150° and decomposed at 156–158°. Identification as (V) was confirmed by analysis, mixed m.p., infrared spectroscopy, and by oxidation with methanolic potash to dithizone.

Diphenylthiocarbazide (V) was also found to be the product of the prolonged action of ammonium hydrogen sulphide on ethanolic solutions of *S*-methyldithizone (III; R = Me) and the sydnone (VII), confirming previous statements by Ogilvie and Corwin.[5]

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Zusammenfassung—Die rote Farbe, die sich beim Zusatz von Mineralsäuren zu Lösungen von Dithizon (I; 3-Mercapto-1,5-diphenylformazan) in gewissen Dioxanproben bildet, rührt im wesentlichen von der Bildung von 2-Methyl-3-phenyl-5-phenylazo-1,3,4-thiadiazolin (II), das sich teilweise von zufällig anwesenden Spuren von 2-Methyldioxolan ableitet. Eine purpurrote Verbindung der Summenformel $C_{13}H_{10}N_4S$ bildet sich auch aus (I) durch eine unabhängige langsamere Reaktion. Aus (I) und Acetaldehyd läßt sich das Thiadiazolin (II) leicht herstellen; analoge Verbindungen von Formaldehyd, Benzaldehyd, Aceton und Äthylmethylketon erhält man in besserer Ausbeute, wenn man von Diphenylthiocarbazid ausgeht. Di-*p*-tolyldithizon gibt ähnliche Reaktionen. Die Reduktion des Thiadiazolins (II) (das Spektren zeigt, die denen der 1:1-Komplexe von (I) mit Arylquecksilber (II)-kationen sehr ähnlich sind) mit Amoniumhydrogensulfid in Äthanol gibt Diphenylthiocarbazid durch Öffnen des Heterorings und Eliminierung eines Alkylrestes aus dem Zwischenprodukt 3-Alkylmercapto-1,5-diphenylformazan. Andere Beispiele nucleophiler Verdrängungen durch SH^- von der Formazangruppe wurden auch untersucht.

Résumé—La coloration rouge qui se développe quand des acides minéraux sont ajoutés à des solutions de dithizone (I, 3-mercapto 1,5-diphénylformazan) dans certains échantillons de dioxane est principalement due à la formation de 2-méthyl-3-phényl-5-phénylazo-1,3,4-thiadiazoline (II) provenant en partie de traces fortuites de 2-méthyldioxalane. Un composé pourpre de formule moléculaire $C_{13}H_{10}N_4S$ se forme aussi à partir de (I) par une réaction indépendante et plus lente. On prépare aisément la thiadiazoline (II) à partir de (I) et d'acétaldéhyde, mais les composés analogues des formaldéhyde, benzaldéhyde, acétone et méthyléthylcétone sont obtenus avec un meilleur rendement en partant du diphénylthiocarbazide. La di-*p*-tolyldithizone donne des réactions semblables. La réduction de la thiadiazoline (II) [qui a un spectre ressemblant exactement à ceux des complexes 1:1 de (I) avec les cations arylmercure (II)] par le sulfure acide d'ammonium en éthanol donne le diphénylthiocarbazide par ouverture de l'hétérocycle et élimination d'un résidu alkyle du 3-alkyl-mercapto 1, 5-diphénylformazan intermédiaire. On a étudié d'autres exemples de déplacements nucléophiles du groupe formazan par SH^-.

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STUDY OF OSMIUM AND RUTHENIUM DISTILLATION WITH RADIOACTIVE TRACERS

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Summary—The distillation characteristics of osmium and ruthenium, which have been studied by using both radioactive tracers and inactive compounds, are reported. The tracer solutions were prepared from hexachloro and hexabromo compounds and from the purified sponges of both metals. A quantitative separation of osmium from ruthenium can be made by distillation from peroxide–sulphuric acid solution at 110° for about 40 min. Slow and incomplete distillations are observed when osmium is present as either the chloro or bromo complex. Optimum conditions for the dissolution of acid-insoluble materials containing osmium and ruthenium are discussed.

THE wet analysis of the six platinum metals usually involves initial selective distillation of the volatile oxides of ruthenium and osmium. Gilchrist[1] reported that the form in which osmium exists in solution has a marked effect on the speed with which it is distilled from nitric acid solutions and that in the form of chloro-osmate, its complete distillation could require as much as 8 hr.

It has also been recorded that the chloro-complexes of osmium and ruthenium offer a peculiar resistance to the quantitative formation of the tetroxides.[2] That the degree of this resistance is a characteristic only in the case of certain oxidants was shown by Westland,[3] who was able to effect complete distillation of the two tetroxides by oxidation of the chloro-complexes with perchloric acid. Recently, Gijbels[4] studied the distillation separation of osmium from ruthenium, using radioactive osmium, and sulphuric acid–hydrogen peroxide mixture as the oxidant. Presumably he found no resistance to complete oxidation.

In the present investigation an effort was made to learn something of the relationship between the forms of osmium and ruthenium salts which responded most readily to complete oxidation to the tetroxide. A special effort was made to arrive at conditions which allowed the quantitative distillation of nanogram amounts of the metals because it was hoped to use the results to establish a method for the direct determination of osmium and ruthenium in ores.

EXPERIMENTAL

Apparatus

Scintillation counter. Nuclear-Chicago model 8725 analyser/scaler incorporated with a single-channel gamma-ray analyser. The detector used was a 2 × 2 in. NaI(Tl) well-type crystal, model 422. A 400-channel gamma-ray analyser, RIDL model 34-27 was used in conjunction with a 3 × 3 in. NaI(Tl) detector.

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Distillation apparatus. A modified form (Fig. 1) of that used by Allan[5] and Gijbels.[4] It became evident during the investigation that the distillation apparatus must be free from contaminants. Prolonged soaking in hot chromic acid mixture, or treatment with chlorine water or organic solvents all failed to clean the apparatus, especially when new equipment was used. It was found that effective cleaning was accomplished by soaking in 10% ethanolic potassium hydroxide solution for about 2 hr. The apparatus was treated by this method after each distillation. Two identical sets of distillation apparatus were used alternatively.

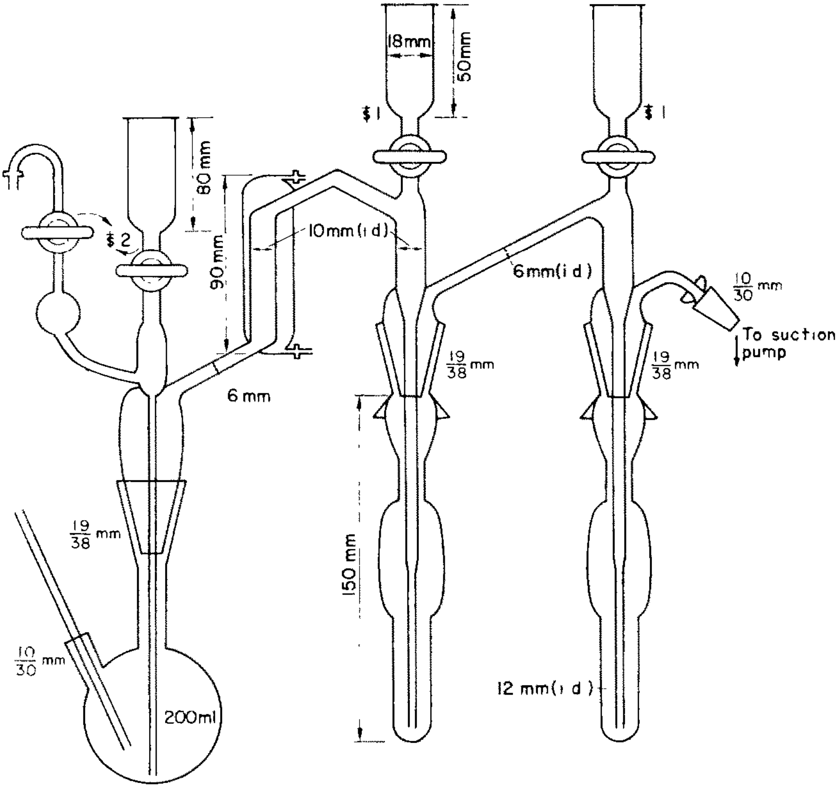

FIG. 1.—Distillation apparatus.

Reagents

Distilled water. Tap water was distilled once in all-glass apparatus and showed no residual activity in the pot liquid when used for distilling radioactive osmium or ruthenium compounds. Water treated with an ion-exchange resin and then distilled, did show residual activity after use in distillation of radioactive compounds, and so was not used.

Thionalide. K & K Laboratories, m.p. 110–111°.

Hydrochloric acid, hydrobromic acid and ethanol. Twice distilled from Pyrex glass apparatus. All other chemicals were of analytical reagent grade.

Purified osmium and ruthenium compounds

The available ammonium hexachlororuthenate and ammonium hexachloro-osmate were found radiochemically to be impure, containing noticeable amounts of iridium, and osmium or ruthenium impurities. The purified salts were prepared by methods modified from those of Gilchrist[6] and Rogers.[7] Ammonium hexachloro-osmate and hexabromo-osmate and osmium sponge were prepared from which six different kinds of osmium tracer solutions were obtained.

Ammonium hexachloro-osmate, $(NH_4)_2OsCl_6$. About 1 g of osmium tetroxide (Johnson Matthey) and 150 ml of twice-distilled 6*M* hydrochloric acid were added to a 500-ml long-neck flask to which a water-cooled condenser was attached. The contents were refluxed for 3 hr. About 6 ml of ethanol were added to achieve complete dissolution. The reddish-brown solution was transferred to a beaker and evaporated to about 200 ml, and then 20 ml of sulphuric acid (1 + 2) were added and the solution was warmed on a water-bath for 2 hr. The brown-black solution was transferred to the distillation flask and diluted to about 200 ml with sulphuric acid (1 + 5). Osmium was distilled for 1·5 hr at 130 ± 5°, during which time about 50 ml of 30% hydrogen peroxide were added dropwise. The distillate was received in three successive receivers containing 150 ml, 25 ml and 25 ml of twice-distilled hydrochloric acid. The trap solution, 25 ml of 5% solution of potassium permanganate, was placed between the distillation flask and the first receiver. The combined receiving solutions were gently refluxed for 2·5 hr, transferred to a beaker and evaporated on a water-bath to a syrup from which the brick red ammonium hexachloro-osmate was precipitated by addition of saturated ammonium chloride solution. The crystals were filtered off on a glass filter, washed with 15% ammonium chloride solution, redissolved in 5 ml of hot azeotropic hydrochloric acid, reprecipitated by addition of 4 ml of 15% ammonium chloride solution to this solution diluted with 6 ml of water, and allowed to stand overnight. The product was filtered off, washed with 95% ethanol until the washings were colourless, then dried over phosphorus pentoxide and ground in a agate mortar. The yield was about 53%. The radiochemical purity of the product was confirmed by gamma-ray spectroscopy.

During the distillation a black ring was sometimes formed around the glass joints of the distillation flask. This proved difficult to remove even by prolonged immersion in *aqua regia*. Remy[8] describes the residue and states that it is insoluble in acids. It was easily removed by immersion in a 1:1 mixture of nitric and sulphuric acids for about 1 hr.

TABLE I.—REDUCTION OF RUTHENIUM AND OSMIUM METALS FROM PURIFIED COMPOUNDS

Salt, *mg*		Sponge obtained, *mg*	Yield, %	Theoretical yield %
$(NH_4)_2OsCl_6$	94·46	Os 40·27	42·63	43·32
$(NH_4)_2OsBr_6$	784·60	Os 211·77	26·99	26·95
$(NH_4)_2RuCl_6$	97·60	Ru 28·13	29·98	29·01

Ammonium hexabromo-osmate, $(NH_4)_2OsBr_6$. This compound was prepared in a similar manner except that hydrobromic acid was used instead of hydrochloric acid. The radiochemical purity was confirmed with the gamma-ray analyser after 35-hr bromine-82 had decayed.

Ammonium hexachlororuthenate, $(NH_4)_2RuCl_6$. The starting material, ammonium hexachlororuthenate, was purified by distilling first with hydrogen peroxide–sulphuric acid as described above to remove its osmium impurity. The ruthenium was then distilled from sodium bromate–sulphuric acid mixture[7] and the salt was crystallized as described for osmium.

Ruthenium and osmium sponge. Weighed amounts of the halide complexes, prepared as above, were reduced to the metals by heating in hydrogen at 500 ± 100° for 3 hr. The results are shown in Table I.

Standard solutions of osmium and ruthenium

About 0·35 g of ammonium hexachlororuthenate or hexachloro-osmate prepared as above was dissolved in 2*M* hydrochloric acid and diluted to 250 ml; the solutions were standardized gravimetrically with thionalide.[7,8] The metal contents of the solutions were: osmium, 0·6126 ± 0·0013 mg/ml; ruthenium, 0·4446 ± 0·0020 mg/ml.

Preliminary experiments

In a preliminary investigation of the distillation pattern, non-radioactive standard solutions of ruthenium and osmium were used. Conditions such as acid concentration, and duration and temperature of the distillation, were varied. Westland's apparatus[9] was used and all the analytical measurements were made by the colorimetric thiourea method, osmium and ruthenium being measured at 480 mμ and 620 mμ respectively. The results are summarized in Table II.

These results indicated that the following factors were of importance for the distillation of these two metals.

1. Osmium and ruthenium, 0·7 mg and 0·2 mg respectively, may be completely distilled within 30 min and 60 min respectively by fuming with perchloric acid.
2. As observed by Gilchrist[1] and Beamish,[2] the speed of osmium distillation becomes noticeably slow if osmium is present as chloro-osmate and the oxidant is a hydrogen peroxide–sulphuric acid mixture used at too low a temperature.
3. The osmium and ruthenium distilled can be completely collected in the first receiver if the rate of hydrogen peroxide addition and the flow-rate of air are carefully controlled.
4. The distillation of osmium tetroxide with hydrogen peroxide–sulphuric acid mixture appears to have a threshold temperature of 105° ± 5°, below which very little can be distilled. The threshold temperature is dependent on the composition of the sulphuric acid–peroxide mixture.

TABLE II.—DISTILLATION OF OSMIUM AND RUTHENIUM

Sample	Oxidant	Temp, °*C*	Time, *min*	Metal added, *μg*	Metal recovered, *μg*	Recovery, %	Receiving solution
$(NH_4)_2OsCl_6$	70% $HClO_4$, 20 ml	150	30	766	760	99·2	2%$(NH_4)_2CS$ in ethanol–HCl
$(NH_4)_2OsCl_6$	70% $HClO_4$, 20 ml	155	15	761	761	99·3	2%$(NH_4)_2CS$ in ethanol–HCl
$(NH_4)_2OsCl_6$ $(NH_4)_2OsCl_6$	conc. H_2SO_4, 20 ml 30% H_2O_2, 40 ml	133	30	766	721	94·1	ice-chilled ethanol–HCl
$(NH_4)_2OsCl_6$	conc. H_2SO_4, 5 ml 30% H_2O_2, 25 ml	110	60	766	333	43·4	ice-chilled ethanol–HCl
$(NH_4)_2OsCl_6$	conc. H_2SO_4, 5 ml	110	60	766	398	51·9	ice-chilled ethanol–HCl
$(NH_4)_2OsCl_6$	12*N* H_2SO_4, 35 ml 30% H_2O_2, 40 ml 12*N* H_2SO_4, 35 ml	105	50	766	574	74·8	ice-chilled ethanol–HCl
$(NH_4)_2OsCl_6$	30% H_2O_2, 40 ml	105	130	766	632	82·5	ice-chilled ethanol–HCl
$(NH_4)_2RuCl_6$	70% $HClO_4$, 20 ml	150	60	211	208	98·6	ethanol–HCl

Distillation with radioactive tracer. Radioactive tracers were used to find the optimum conditions for distillation of micro and semi-micro amounts, especially for osmium; ruthenium always showed better consistency in recovery.

The osmium tracer solutions were prepared from the irradiated starting materials by methods summarized in Table III. Silica ampoules, containing about 10 mg of purified osmium or ruthenium, were irradiated for 3 days at a flux of approximately 5×10^{12} n. cm^{-2}. sec^{-1} in the McMaster University Reactor (Hamilton, Ontario, Canada). After a cooling period of about 5 days, the irradiated materials, except osmium tetroxide, were thoroughly mixed in a nickel crucible with about 0·8 g of freshly opened sodium peroxide and fused with a Meker burner for about 5 min. The fused mass was disintegrated first with water and then with 1*N* hydrochloric or sulphuric acid, and diluted to 100 ml with 5*N* hydrochloric or sulphuric acid. (Table III, Types *C*, *D*, *E*, *F*.) The ruthenium tracer solution showed gamma peaks of 40-day ^{103}Ru at 498 and 615 keV, while the osmium solution showed the gamma-peaks of 15-day ^{191}Os at 45 and 130 keV and of 94-day ^{185}Os at 646 and 875 keV.

Osmium or ruthenium tracer solutions (5 ml; $\sim 3 \times 10^5$ cpm) were placed in the distillation flask together with the amounts of sulphuric acid shown in Table IV, and 20 ml of 30% hydrogen peroxide. Five ml of 9*M* sodium hydroxide were placed in each of the two receivers. The flask was

TABLE III.—TYPES OF OSMIUM TRACER SOLUTIONS

Type	Compound irradiated	Na_2O_2 fusion	Acid used for dissolution
A	Osmium tetroxide	No	HCl
B	Osmium tetroxide	No	H_2SO_4
C	$(NH_4)_2OsBr_6$	Yes	HCl
D	$(NH_4)_2OsBr_6$	Yes	H_2SO_4
E	Os sponge	Yes	HCl
F	Os sponge	Yes	H_2SO_4

A. After dissolution in HCl, osmium tetroxide was distilled with H_2SO_4–H_2O_2 and received in NaOH solution, which was then acidified with HCl and diluted to 50 ml.

B. Tracer *A* solution was three times evaporated to fumes with sulphuric acid (chloride-free) and diluted to *ca*. 30 ml with 5*N* sulphuric acid. Some of the original activity was lost during the evaporations.

C. Used after ^{82}Br had decayed.

electrically heated with a mantle while a current of air was drawn slowly (2–5 bubbles/sec) through the apparatus. During the distillation period, 5–40 ml of 30% hydrogen peroxide were added dropwise to the distillation flask (to give the total volume shown in Table IV). The distillate collected in the receivers, with the water-washings, was transferred to a 25-ml volumetric flask and diluted with water to volume. The activity of the distillate was measured with a scintillation counter (a single-channel analyser). The liquid remaining in the distillation flask was diluted to 25 ml and its activity was measured similarly. The total activity, *i.e.*, the sum of the activities of the distillate and that left in the flask was consistent with that taken. The distillation apparatus was reduced in size as shown in Fig. 1 in order to be applicable to the range 1–100 μg.

TABLE IV.—DISTILLATION OF OSMIUM (TRACER AMOUNT WITHOUT CARRIER ADDED)

Expt. no.	Type of tracer	Tracer amount, *μg*	Oxidant		Temp, °*C*	Duration, *min*	Residual activity*	Distilled %
			H_2SO_4 *ml*	30% H_2O_2, *ml*				
1	A	70	conc., 35	25	104 ± 20	22	Yes	98·0
2	A	70	conc., 25	25	110 ± 10	35	Yes	90·0
3	A	70	conc., 25	28	127 ± 5	35	Yes	95·0
4	A	20	12*N*, 40	25	106 ± 4	35	Yes	50·0
5	B	20	12*N*, 40	25	104 ± 20	45	Yes	80·0
6	C	10	12*N*, 40	60	105 ± 4	43	Yes	96·0
7	C	10	12*N*, 40	60	105 ± 2	60	Yes	95·0
8	D	10	12*N*, 40	40	105 ± 2	30	Yes	60
9	D	10	12*N*, 40	50	107 ± 5	45	Yes	96
10	D	10	12*N*, 40	50	107 ± 5	47	Yes	97
11	E	3·2	12*N*, 40	50	105 ± 2	63	Yes	94
12	E	1·6	12*N*, 40	50	106 ± 2	100	Yes	96
13	F	10	12*N*, 40	50	105 ± 4	120	No	99·2
14	F	10	12*N*, 40	50	106 ± 2	60	No	98·8
15	F	10	12*N*, 40	50	107 ± 5	60	No	99·2
16	F	5	12*N*, 40	50	105 ± 2	45	No	99·8
17	F	5	12*N*, 40	50	105 ± 3	35	No	99·0†
18	F	5	12*N*, 40	50	105 ± 2	35	No	100·6‡
19	F	55	12*N*, 40	50	105 ± 3	40	No	100·3§

* The activities remaining in the flask after distillation.

† No hydrochloric acid was added to the pot.

‡ Hydrochloric acid (6*M*, 2 ml) added to the pot.

§ Hydrochloric acid (6*M*, 2 ml) and osmium tracer mixed and allowed to stand overnight before distillation.

In experiments 1–5 (Table IV) less peroxide was added because of its very vigorous decomposition at higher temperature. Experiment 5 showed the effect of previously converting the chloro-complex into the sulphate. In the other experiments more peroxide than necessary was added, to allow adaptation of the process for analysis of ore samples.

From the results in Table IV, it appeared that the conditions for experiment 19 were best. To determine whether ruthenium was co-distilled under these conditions,[5] three aliquots of ruthenium tracer solution, each containing about 10 μg of the metal, were distilled. It was found that the amount of active ruthenium distilled (< 0·2 μg) was negligible, and it was concluded that ruthenium is quantitatively retained. As in distillation of inactive osmium and ruthenium, both metals were always completely collected in the first receiver, containing 5 ml of 9*M* sodium hydroxide.

DISCUSSION

It is evident from Tables II–IV that when chloro-osmate is the starting material, complete distillation of osmium requires an extended period. However, as shown in experiments 17, 18, 19, a small amount of hydrochloric acid has no retarding effect on the distillation of osmium initially present as sulphate species. It therefore seems probable that the important factor in preparing an osmium sample for distillation is the type of acid used to dissolve the sample after the peroxide fusion.

It was originally expected that if all of the standard osmium materials were fused with sodium peroxide and dissolved with sulphuric acid, the product would show the same properties irrespective of the original forms. However, as shown in Table IV, the distillation characteristics of the original osmium form seem to be retained.

These findings are in conflict with Gijbel's, in contrast to which it was noted by the present authors that if the irradiated osmium sponge was fused with sodium peroxide and the black suspension from the water-leached product was acidified with hydrochloric acid, the osmium was not quantitatively distilled from the peroxide–sulphuric acid solution (see experiments 11 and 12 in Table IV). However, the difference in results may have been caused by the lesser amount of hydrochloric acid used by Gijbels for the dissolution of osmium.

As shown in the distillations 13–19 (Table IV). the only form of osmium prepared by the authors which gives complete distillation of the tetroxide from sulphuric acid–peroxide mixture in the time indicated in Table IV is that in tracer *F*. This fact will be of some importance when osmium or ruthenium are to be determined directly in ores.

This approach is of course dependent on the use of the peroxide–sulphuric acid method for the selective isolation of osmium and ruthenium from ores and concentrates.[10] Nitric acid is the most commonly used reagent for the preliminary removal of osmium, but it effectively interferes in the removal of ruthenium. Perchloric acid is also avoided because no proven method has yet been recorded for the determination of the remaining platinum metals in a perchloric acid medium containing base metals (though a solution to this problem will be reported later) and because it oxidizes both osmium and ruthenium.

Zusammenfassung—Die Destillationseigenschaften von Osmium und Ruthenium, die mit radioaktiven Tracern und inaktiven Verbindungen untersucht wurden, werden mitgeteilt. Die Tracerlösungen wurden aus den Hexachloro- und Hexabromoverbindungen sowie aus den gereinigten schwammförmigen Metallen hergestellt. Osmium kann von Ruthenium quantitativ getrennt werden durch 40-min Destillation aus einer Lösung mit Peroxid und Schwefelsäure bei 110°C. Ist Osmium als Chloro- oder Bromokomplex anwesend, so beobachtet man langsame und unvollständige Destillation. Die optimalen Bedingungen zum Lösen von Osmium und Ruthenium enthaltenden säureunlöslichen Materialien werden diskutiert.

Résumé—On décrit les caractéristiques de distillation de l'osmium et du ruthénium, qui ont été étudiées en utilisant tant des traceurs radioactifs que des composés inactifs. Les solutions de traceurs ont été préparées à partir d'hexachloro et d'hexabromo composés et à partir des mousses purifiées des deux métaux. On peut affectuer une séparation quantitative de l'osmium du ruthénium par distillation à partir d'une solution peroxyde–acide sulfurique à 110° pendant environ 40 mn. On observe des distillations lentes et incomplètes lorsque l'osmium est présent à l'état de chloro- ou bromocomplexe. On discute des conditions optimales pour la dissolutions de substances acido-insolubles contenant de l'osmium et du ruthénium.

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SPEKTRALPHOTOMETRISCHE UNTERSUCHUNG DER REAKTION VON BARIUMIONEN MIT SULFONAZO III

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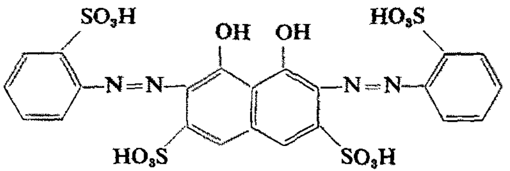
(*Eingegangen am* 2. *Oktober* 1967. *Angenommen am* 12. *Januar* 1968)

Zusammenfassung—Der molare Extinktionskoeffizient des Bariumkomplexes von Sulfonazo III (ML-Typ) beträgt $6{,}45 \cdot 10^4$ bei 642 nm, der differentielle Extinktionskoeffizient bei pH 1,9–2,8 $5{,}0 \cdot 10^4$. Die auf Grund starker Dissoziation des Komplexes bei der Bariumbestimmung praktisch anwendbare effektive Extinktionskoeffizienten bewegen sich etwa von 1,5 bis $4{,}0 \cdot 10^4$ in Abhängigkeit von pH und totaler Sulfonazo III -Konzentration. Es wurden die Beständigkeitskonstanten des Komplexes bei pH 1,7–3,7 bestimmt und seine Zusammensetzung überprüft. Eine neue Methode zur Bestimmung von Extinktionskoeffizienten bei kleinen Metallkonzentrationen und verschiedenen Komplexbildnerkonzentrationen wurde entwickelt und überprüft.

DIE von uns entwickelten Methoden zur coulometrischen titanometrischen Gehaltsbestimmung[1] und Reinheitskontrolle einiger Bisazoderivate der Chromotropsäure[2] ermöglichten die Untersuchung der Komplexbildung von Sulfonazo III (2,7-Bis[azo-2-sulfophenyl]chromotropsäure, siehe Strukturformel) mit Barium. Die analytische Verwendung von Sulfonazo III wurde bisher bei der spektralphotometrischen Bariumbestimmung sowie bei volumetrischen Sulfatbestimmungen mit Bariumionen als Indicator beschrieben.[3,4] Bei gründlichem Studium am chromatographisch reinen Sulfonazo III[2] konnten wir neue Werte der molaren Extinktionskoeffizienten sowie der Komplexbildungskonstante feststellen, die von den bisher angegebenen[3] beträchtlich abweichen. Da es sich um einen verhältnismäßig dissoziierten Komplex mit einem hohen Wert des molaren Extinktionskoeffizienten handelt, ein Fall, der bei der analytischen Ausnutzung der Komplexbildung nur selten vorkommt und darum wenig untersucht wird, haben wir uns näher der Bestimmung der Zusammensetzung des Komplexes sowie den Methoden der Bestimmung der Bildungskonstante und des molaren Extinktionskoeffizienten gewidmet.



Sulfonazo III

THEORETISCHER TEIL

Verwendete Symbole und Grundbeziehungen

c_M, c_L totale Metall- bzw. Ligand-Konzentrationen molar
K Beständigkeitskonstante

$$K = \frac{[M_aL_b]}{[M]^a[L]^b}\,. \tag{1}$$

Für die Gleichgewichtskonzentrationen [M], [L], $[M_aL_b]$ gilt:

$$[M] = c_M - a[M_aL_b] \tag{1a}$$

$$[L] = c_L - b[M_aL_b]. \tag{1b}$$

A Extinktion bei der Schichtdicke 1 cm (Extinktionsmodul)
ΔA differentielle Extinktion, gemessen gegen Blindversuch
ε_L, ε_M, $\varepsilon_{M_aL_b}$ molare Extinktionskoeffizienten
Bei $\varepsilon_M \to 0$ gilt:

$$A = \varepsilon_{M_aL_b} \cdot [M_aL_b] + \varepsilon_L \cdot [L] = \varepsilon_{M_aL_b} \cdot [M_aL_b] + \varepsilon_L c_L - b \cdot \varepsilon_L \cdot [M_aL_b] \tag{2}$$

und

$$A - \varepsilon_L c_L \equiv \Delta A = [M_aL_b] \cdot (\varepsilon_{M_aL_b} - b \cdot \varepsilon_L) = [M_aL_b] \cdot \Delta\varepsilon_{M_aL_b}. \tag{2a}$$

$\Delta\varepsilon_{M_aL_b}$ wird als differentieller molarer Extinktionskoeffizient bezeichnet.

Neben dieser Grösse definieren wir noch einen effektiven differentiellen molaren Extinktionskoeffizienten $\Delta\varepsilon_{M_aL_b},_{\text{eff}}$:

$$\Delta\varepsilon_{M_aL_b},_{\text{eff}} = a \cdot \Delta A/c_M \quad \text{für } a \cdot c_M < b.c_L, \tag{3}$$

bzw.

$$\Delta\varepsilon_{M_aL_b},_{\text{eff}} = b \cdot \Delta A/c_L \quad \text{für } a \cdot c_M > b.c_L. \tag{3a}$$

Transformation der photometrischen Titrationskurven

Bei einem grossen Metallüberschuß ($c_M \gg c_L$) sind praktisch sämtliche Liganden im Komplex gebunden:

$$[M_aL_b] = c_L/b. \tag{4}$$

Für den Grenzwert von ΔA auf dem horizontalen Ast der Titrationskurve (ΔA_0) gilt dann:

$$\Delta A_0 = \Delta\varepsilon_{M_aL_b} \cdot c_L/b \tag{5}$$

Daraus kann unmittelbar der Wert von $\Delta\varepsilon_{M_aL_b}$ bestimmt werden. Nach dem Einsetzen in die Beziehung (1), Logarithmieren und nach der Vereinfachung erhält man im Fall eines ML-Komplexes die Gleichung einer Gerade:

$$\log \frac{1}{c_M/c_L \cdot \Delta A_0 - \Delta A} = -\log \frac{\Delta A}{\Delta A_0 - \Delta A} + k. \tag{6}$$

Ähnliche Beziehungen können auch für Komplexe anderer Zusammensetzung (M_aL_b) abgeleitet werden. Als Beweis der Bildung des gesuchten Komplexes gilt der lineare Verlauf der transformierten Titrationskurve in den entsprechenden Koordinaten.

Für den Komplex ML hat die Konstante k der Geraden den Wert:

$$k = \log K - \log \Delta\varepsilon_{ML}. \tag{6a}$$

Bei bekanntem $\Delta\varepsilon_{ML}$ (aus ΔA_0, vgl. oben) läßt sich daraus der Wert von K berechnen.

Bestimmung von $\Delta\varepsilon_{ML_b}$ und K bei nicht stabilen Komplexen

Die Gleichung für K kann umgeformt werden (aus 1, 1*a* und 1*b*):

$$(c_M - a \cdot [M_aL_b])^a \cdot (c_L - b \cdot [M_aL_b])^b - [M_aL_b]/K = 0. \tag{1c}$$

Es ist sinnvoll daraus den Ausdruck $d[\mathrm{M}_a\mathrm{L}_b]/d\,c_\mathrm{M}$ für c_L = konst. zu berechnen:

$$\left(\frac{d[\mathrm{M}_a\mathrm{L}_b]}{d\,c_\mathrm{M}}\right)_{c_\mathrm{L}=\mathrm{konst.}} = \frac{a(c_\mathrm{M} - a[\mathrm{M}_a\mathrm{L}_b]^{a-1} \cdot (c_\mathrm{L} - b[\mathrm{M}_a\mathrm{L}_b])^b}{a^2(c_\mathrm{M} - a[\mathrm{M}_a\mathrm{L}_b])^{a-1} \cdot (c_\mathrm{L} - b[\mathrm{M}_a\mathrm{L}_b])^b + b^2(c_\mathrm{M} - a[\mathrm{M}_a\mathrm{L}_b])^a \cdot (c_\mathrm{L} - b[\mathrm{M}_a\mathrm{L}_b])^{b-1} + 1/K} \tag{7}$$

Der Richtungskoeffizient der Tangente der Funktion

$$[\mathrm{M}_a\mathrm{L}_b] = \mathrm{f}(c_\mathrm{M})$$

bei konstanter c_L für lim $c_\mathrm{M} \to 0$ (Anfang der photometrischen Titrationskurve eines Ligands durch Kation) ist bei einkernigenkomplexen (ML_b) gegeben durch Beziehung:

$$\lim \left(\frac{d[\mathrm{ML}_b]}{d\,c_\mathrm{M}}\right)_{c_\mathrm{M}\to 0} = \frac{c_\mathrm{L}{}^b}{c_\mathrm{L}{}^b + 1/K}. \tag{8}$$

Nach der Einführung der photometrischen Meßgrössen für $[\mathrm{ML}_b]$ erhält man:

$$\lim \left(\frac{d\,\Delta A}{d\,c_\mathrm{M}}\right)_{c_\mathrm{M}\to 0} \equiv \Delta\varepsilon_{\mathrm{ML}_b,\mathrm{eff}} = \Delta\varepsilon_{\mathrm{ML}_b} \cdot \frac{c_\mathrm{L}{}^b}{c_\mathrm{L}{}^b + 1/K}. \tag{9}$$

Nach weiterer Umformung ergibt sich eine für die graphische Lösung der gegebenen Aufgabe geeignete Gleichung:

$$c_\mathrm{L}{}^b = \Delta\varepsilon_{\mathrm{ML}_b} \cdot c_\mathrm{L}{}^b/\Delta\varepsilon_{\mathrm{ML}_b,\mathrm{eff}} - 1/K. \tag{10}$$

$\Delta\varepsilon_{\mathrm{ML}_b,\,\mathrm{eff}}$ sind die aus den linear verlaufenden ansteigenden Anfangsabschnitten der photometrischen Titrationskurven für die entsprechenden c_L errechneten Werte. In einem Diagramm $c_\mathrm{L}{}^b$ gegen $c_\mathrm{L}{}^b/\Delta\varepsilon_{\mathrm{ML}_b,\mathrm{eff}}$ gibt der Richtungskoeffizient der resultierenden Gerade den gesuchten Werte $\Delta\varepsilon_{\mathrm{ML}_b}$. Der negativ genommene Abschnitt der $c_\mathrm{L}{}^b$-Achse liefert den Kehrwert der Beständigkeitskonstante K.

In der Abb. 1 ist die Abhängigkeit $\Delta\varepsilon_{\mathrm{ML},\mathrm{eff}}$ von der Konstante K angegeben.

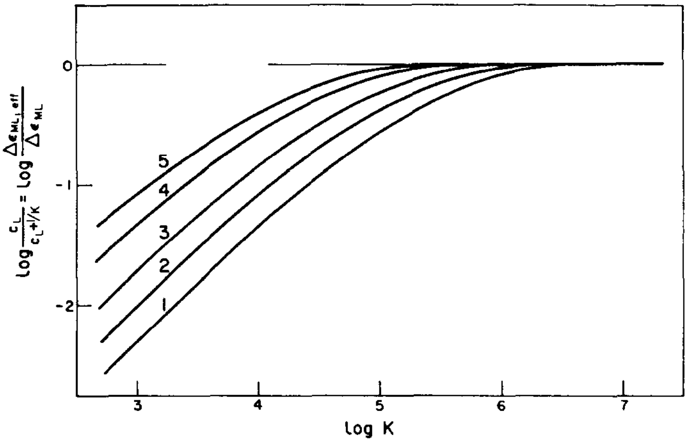


ABB. 1.—Abhängigkeit des Koeffizientes $\Delta\varepsilon_{\mathrm{ML},\mathrm{eff}}$. von K.
$c_\mathrm{L} = 5 \cdot 10^{-6}M$ *1*; $c_\mathrm{L} = 1 \cdot 10^{-5}M$ *2*; $c_\mathrm{L} = 2 \cdot 10^{-5}M$ *3*; $c_\mathrm{L} = 5 \cdot 10^{-5}M$ *4*; $c_\mathrm{L} = 1 \cdot 10^{-4}M$ *5*.

Hieraus lassen sich die Grenzen der praktischen Anwendbarkeit der Beziehung (10) ablesen. Analoge Diagramme werden auch für Komplexe ML_b mit $b > 1$ erhalten.

Aus Beziehung (10) geht hervor, daß die Kenntnis von c_L für die Bestimmung von $\Delta\varepsilon_{ML_b}$ nicht notwendig ist; es genügt eine konzentriertere Lösung des untersuchten Komplexbildners in bekannten Verhältnissen zu verdünnen.

Eine analoge Beziehung zu (10) kann auch für Komplexe M_aL, die bei einem großen Metallüberschuß entstehen, abgeleitet werden:

$$c_M{}^a = \Delta\varepsilon_{M_aL} \cdot c_M{}^a / \Delta\varepsilon_{M_aL,\text{eff}} - 1/K. \tag{11}$$

$\Delta\varepsilon_{M_aL,\text{eff}}$ bedeutet hier den Richtungskoeffizienten der photometrischen Titrationskurve des Kations mit dem Ligand für $c_L \rightarrow 0$.

Die abgeleitete Beziehung zwischen $\Delta\varepsilon_{ML_b,\text{eff}}$ und c_L ist für die analytische Praxis sehr bedeutungsvoll, da die Werte von $\Delta\varepsilon_{ML_b,\text{eff}}$ gleichzeitig die Richtungskoeffizienten der Eichkurven bei den photometrischen Bestimmungen bilden.

EXPERIMENTELLER TEIL

Chemikalien und Geräte

Für alle Untersuchungen wurde chromatographisch reines Sulfonazo III (freie Säure)[2] verwendet; die Ergebnisse wurden mit den handelsüblichen Produkten von Sulfonazo III *p.a.*, LACHEMA Brno, (Natriumsalze) überprüft. Die Konzentrationen der Stammlösungen von Sulfonazo III (etwa $1 \cdot 10^{-3}M$) wurden coulometrisch bestimmt.[1]

Die Bariumionen wurden in Form einer Bariumnitratlösung zugegeben. Die Konzentration der Stammlösung ($0{,}05M$) wurde komplexometrisch bestimmt.

Alle verwendete Chemikalien waren analysenrein.

Die spektralphotometrischen Messungen wurden auf dem registrierenden Spektralphotometer CF 4, Optica Milano, in 0,2 bis 2,0-cm Küvetten durchgeführt. Bei den angegebenen Werten handelt es sich stets um Extinktionsmodule. Die Wellenlänge der Messung betrug, falls nichts anderes angegeben wird, 642 nm, wo das differentielle Absorptionsspektrum ein Maximum aufweist.

Einfluß von pH

Es wurden Absorptionskurven von $1 \cdot 10^{-5}M$ Sulfonazo III-Lösungen gegen Wasser vermessen. Die Acidität der Lösungen wurde durch kleine Zugaben von etwa $2M$ Perchlorsäure, bzw. $2M$ Natronlauge eingestellt. Einige der gewonnenen Kurven sind auf der Abb. 2 abgebildet.

Für die Untersuchung des pH-Einflusses auf die Bildung des Bariumkomplexes wurde analog verfahren: Durch Zugaben von Perchlorsäure wurde die Acidität einer $5 \cdot 10^{-5}M$ Lösung von Sulfonazo III eingestellt. Von dieser Lösung wurden je 20 ml in zwei 25-ml Meßkolben abgemessen und in einen der beiden Meßkolben zusätzlich 2,5 ml einer neutralen $2 \cdot 10^{-4}M$ Bariumnitratlösung gegeben. Nach Auffüllen und Kontrolle des pH-Wertes wurden Spektren der bariumhaltigen Lösungen gegen die Blindlösungen aufgenommen. Aus den maximalen Werten von ΔA, die stets bei 642 nm lagen, wurden unter Annahme, daß $\Delta\varepsilon_{ML} = 5 \cdot 10^4$ und daß ein Komplex des Typus ML entsteht (vgl. weiter), die Konstanten K errechnet Abbildung 3 gibt deren pH-Abhängigkeit wieder.

Bei einem konstanten pH-Wert (2,80, mit Essigsäure, bzw. 2,29, mit Perchlorsäure eingestellt) und einem konstanten Verhältnis von c_M und c_L wurden die Abhängigkeiten $\Delta A = f(c_L)$ untersucht. Für einen gegenseitigen Vergleich sind die gewonnenen Werte von ΔA auf $\Delta\varepsilon_{ML,\text{eff}}$ umgerechnet, und in Abb. 4 zusammengestellt.

Photometrische Titrationskurven

Es wurden Abhängigkeiten $\Delta A = f(c_M)$ bei $c_L = \text{konst.}$ ($2\text{–}10 \cdot 10^{-5}M$) in $0{,}1M$ Essigsäure (pH 2,80), bzw. in Britton–Robinsonschem Puffer pH 1,9(10 ml pro 25 ml, $c_{Na} = 2 \cdot 10^{-3}M$)gemessen. Die erhaltenen Werte sind in der Abb. 5 aufgetragen. Erst bei einem etwa 50 fachen Bariumüberschuß sind die ΔA-Werte von c_M unabhängig und betragen 1,0 bei $c_L = 2 \cdot 10^{-5}M$ (Abb. 5, Kurve *1*) 2,5 bei $c_L = 5 \cdot 10^{-5}M$ (Kurve *2*), und 5,0 bei $c_L = 1 \cdot 10^{-4}M$ (Kurve *3*). Die ausgezogenen Kurven in der Abb. 5 wurden für den weiter abgeleiteten Wert von $\Delta\varepsilon_{ML}$ $5 \cdot 10^4$ und für $K = 4{,}3 \cdot 10^4$ berechnet. Die Richtungskoeffizienten der Tangenten t_1, t_2, t_3 (Abb. 5) betrugen $2{,}3 \cdot 10^4$; $3{,}2 \cdot 10^4$ und $4{,}0 \cdot 10^4$ ($\equiv \Delta\varepsilon_{ML,\text{eff}}$ für $c_M \rightarrow 0$).

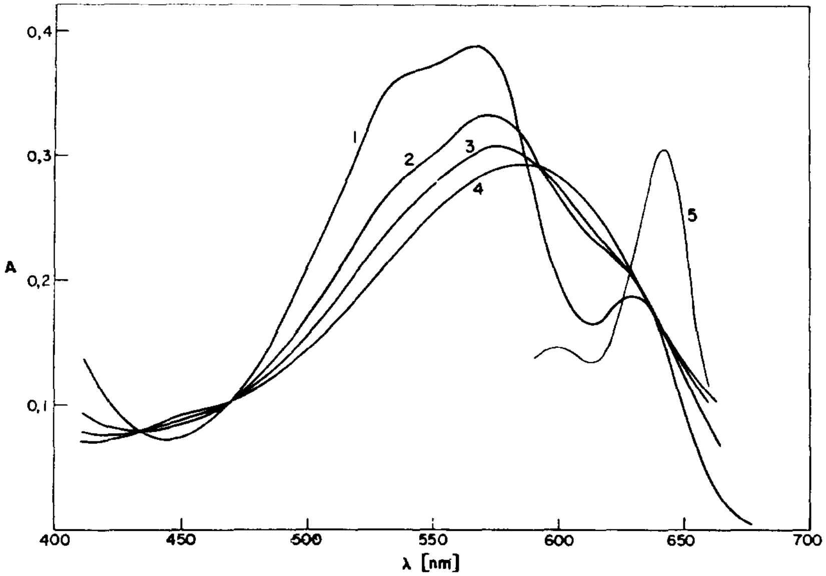


Abb. 2.—Absorptionskurven.
Kurven 1–4 gegen Wasser; $c_L = 1 \cdot 10^{-5} M$.
1—pH 2,04 gilt auch für pH 1,5 bis 3,5; 2—pH 10,7;
3—pH 11,4; 4—pH 12,0.
5—differentielle Absorptionskurve bei Ba-Bestimmung (ΔA gegen λ)
$c_L = 1 \cdot 10^{-4} M$, $c_M = 8 \cdot 10^{-6} M$, pH 2,80.

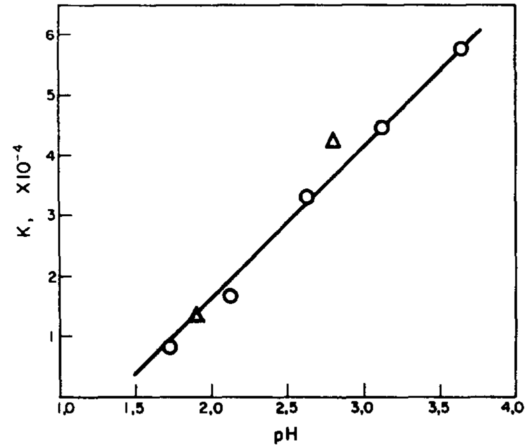


Abb. 3.—pH-Abhängigkeit von Beständigkeitskonstanten. Δ aus photometrischen Titrationen abgeleitete Werte.

Jobsche Kurve

Die photometrische Untersuchung der kontinuierlichen Variationen in isomolaren Lösungen wurde in $0{,}1 M$ Essigsäure (pH 2,80) bei $c_M + c_L = 8 \cdot 10^{-5} M$ vorgenommen. Die Ergebnisse der Messungen gegen die entsprechenden Blindlösungen sind aus Abb. 6 ersichtlich. Die ausgezogene Kurve wurde für $\Delta\varepsilon_{ML} = 5 \cdot 10^4$ und $K = 4{,}3 \cdot 10^4$ berechnet.

Störung durch Natrium- und Calciumionen

Der Einfluß von Natrium- und Calciumchlorid-Zugaben auf die Komplexbildung wurde in $0{,}1 M$ Essigsäure (pH 2,80) untersucht. Bei den Messungen war $c_L = 1.04 \cdot 10^{-5} M$ und $c_M = 4 \cdot 10^{-6} M$

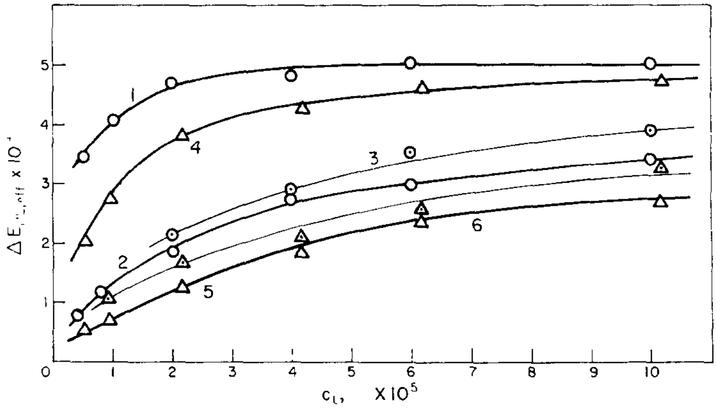


ABB. 4.—Effektive Extinktionskoeffizienten in Abhängigkeit von c_L. Kurven *1–3* pH 2,80 Essigsäure, Kurven *4–6* pH 2,30 Perchlorsäure. *1* und *4*—$c_M/c_L = 12$; *2* und *5*-$c_M/c_L = 1{,}2$; *3* und *6*—$c_M/c_L = 0{,}12$.

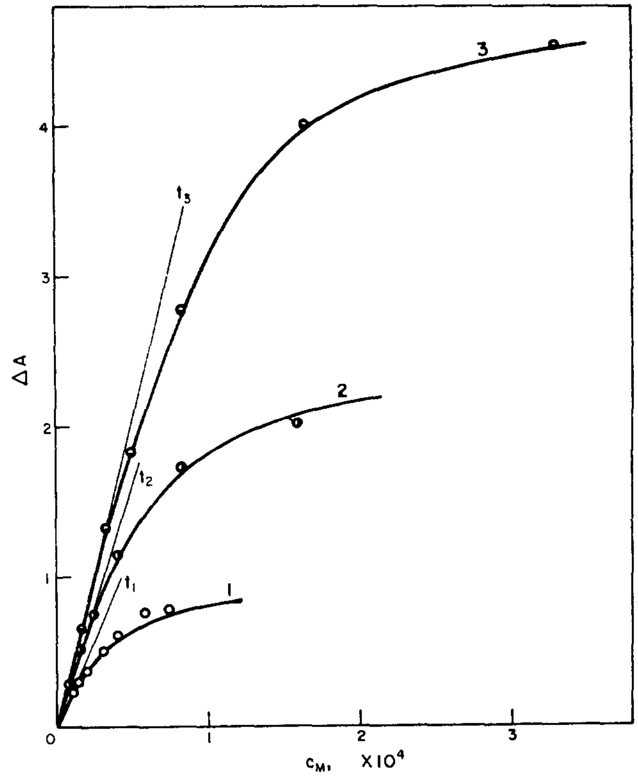


ABB. 5.—Photometrische Titrationskurven. pH 2,80; *1*—$c_L = 2 \cdot 10^{-5}M$; *2*—$c_L = 5 \cdot 10^{-5}M$; *3*—$c_L = 1 \cdot 10^{-4}M$. t_1, t_2, t_3—Tangenten der Kurven *1–3* für $c_M \to 0$. Ausgezogene Kurven wurden berechnet.

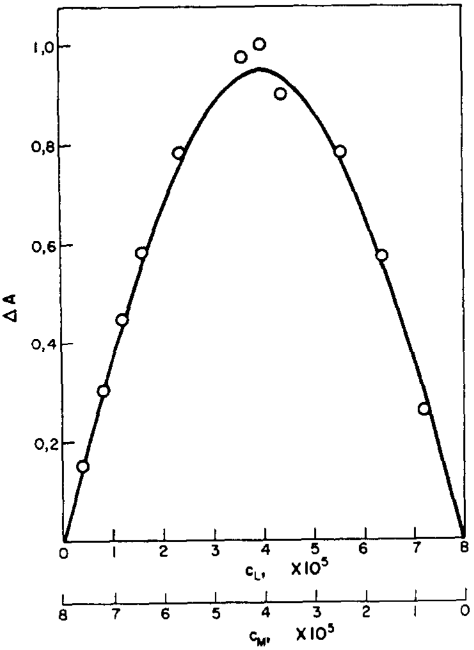


Abb. 6.—Jobsche Kurve.
pH 2,80; $c_M + c_L = 8 \cdot 10^{-5}M$. Ausgezogene Kurve wurde berechnet.

(Kurven *3*, *4* und $\Delta_{4,5}$, Abb. 7) bzw. $c_M = 8 \cdot 10^{-5}M$ (Kurven *1* und $\Delta_{1,2}$). Die aus den horizontalen Ästen der Kurven $\Delta_{1,2}$ bzw. $\Delta_{3,2}$ und $\Delta_{4,5}$ berechneten Werte von $\Delta\varepsilon_{ML,eff}$ betragen bei Annahme eines Komplexes des Typus ML $4 \cdot 10^4$ bzw. $1{,}4 \cdot 10^4$.

DISKUSSION

Die Bildung eines Komplexes von Sulfonazo III mit Bariumionen macht sich bei Steigerung der Bariumkonzentration durch Erhöhung der Absorptionsbande mit einem Maximum bei 642 ± 2 nm auf dem differentiell aufgenommenen Spektrum bemerkbar, d.h. bei Wellenlängen, bei welchen sich die Absorption von reinem Sulfonazo III rasch ändert.[2] Der Wert von ε_L bei dieser Wellenlänge beträgt $1{,}45 \cdot 10^4$. Infolge dieses hohen Wertes ist es notwendig, alle Messungen differenziell gegen die entsprechenden Blindlösungen auszuführen.

Neben dem Hauptmaximum bei 642 nm kann man auf den Spektren noch ein Nebenmaximum bei 600 nm (Abb. 2, Kurve *5*) beobachten. Das Verhältnis der Extinktionen $\Delta A_{642}/\Delta A_{600}$ ist konstant und beträgt 2,1.

Aus den vermessenen Absorptionsspektren bei verschiedenen pH-Werten (Abb. 2) ist ersichtlich, daß in dem pH-Gebiet 2 bis 3, in welchem die Bestimmungen ausgeführt werden, praktisch keine Änderungen der Absorption auftreten. Deshalb konnten wir auch nicht die Dissoziationsgleichgewichte von Sulfonazo III bei diesen pH-Werten photometrisch untersuchen und somit die Gültigkeit der früher von Buděšínský angegebenen[3] Dissoziationskonstanten überprüfen. Wir beschränkten uns auf die Bestimmung von Beständigkeitskonstanten *K*, die die Verhältnisse in den gegebenen Systemen vollkommen ausdrücken, wobei für [L] die Differenz c_L—[ML] (Komplex 1:1) eingesetzt wurde. Die meisten Untersuchungen wurden dann bei pH 2,80 (0,1*M* Essigsäure) ausgeführt.

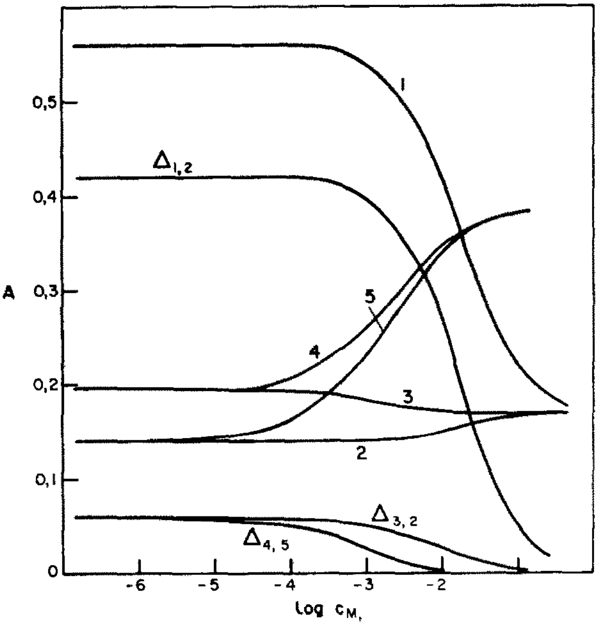


ABB. 7.—Störung von Natrium- und Calciumionen.
pH 2,80; $c_L = 1,04 \cdot 10^{-5} M$; *1–3*—Abhängigkeit von c_{Na^+}; *4* und *5*—Abhängigkeit von $c_{Ca^{2+}}$. Kurven *1–5*g emessen gegen Wasser, $\Delta_{1,2}$, $\Delta_{3,2}$, $\Delta_{4,5}$—Differenz der entsprechenden Kurven.
1—$c_M = 8 \cdot 10^{-5} M$; *3* und *4*—$c_M = 4 \cdot 10^{-6} M$; *2* und *5*—Blindwerte.

Die Zusammensetzung des entstehenden Komplexes wurde in isomolaren Lösungen bei pH 2,80 untersucht (Jobsche Kurve). Das Verhältnis Metall—Komplexbildner ist 1:1; aus der Form der Kurve (gemessen im Absorptionsmaximum 642 nm) ergibt sich, daß ein stark dissoziierter Komplex vorliegt.

Um die Bildung eines einkernigen Komplexes des Typus ML zu bestätigen, wurden die photometrischen Titrationskurven (pH 2,80, Abb. 5) in eine Gerade transformiert, wobei gleichzeitig der Wert von K bestimmt werden konnte. Bei einem schwachen Komplex, der bei Wellenlängen absorbiert, bei welchen selbst der Komplexbildner eine beträchtliche Absorption aufweist, kann die logarithmische Analyse mit den angenommenen Vereinfachungen (vgl. z.B.[5]) nicht angewandt werden. Es ist im Gegenteil notwendig, die Messungen bei vergleichbaren Konzentrationen c_L und c_M vorzunehmen. Deshalb wurde die oben abgeleitete Beziehung (6) benutzt. Es ist die Gleichung einer Gerade, die in den entsprechenden Koordinaten durch den Richtungskoeffizienten -1 charakterisiert ist. Aus dem Ordinatenabschnitt kann K berechnet werden. Es ist günstig, daß die Messpunkte an beiden Seiten des extrapolierten Wertes liegen. $\Delta\varepsilon_{ML}$ wird mit Hilfe von ΔA_0 bestimmt (nach (5)).

Die Ergebnisse der Transformation der drei photometrischen Titrationskurven bei pH 2,80 ($c_L = 2$; 5 und $10 \cdot 10^{-5} M$, vgl. Abb. 5) sind aus der Abb. 8 ersichtlich. Aus dem identischen linearen Verlauf der transformierten Kurven folgt, daß in dem ganzen untersuchten Konzentrationsgebiet ($c_L = 2$ bis $10 \cdot 10^{-5} M$, c_M $5 \cdot 10^{-6}$ bis $1 \cdot 10^{-2} M$) nur ein Komplex des Typus ML entsteht. Der experimentell bestimmte Wert des Richtungskoeffizienten beträgt —0,97 und der Wert der Beständigkeitskonstante K $(4,3 \pm 0,2) \cdot 10^4$. Der aus ΔA_0 abgeleitete Wert von $\Delta\varepsilon_{ML}$ beläuft sich

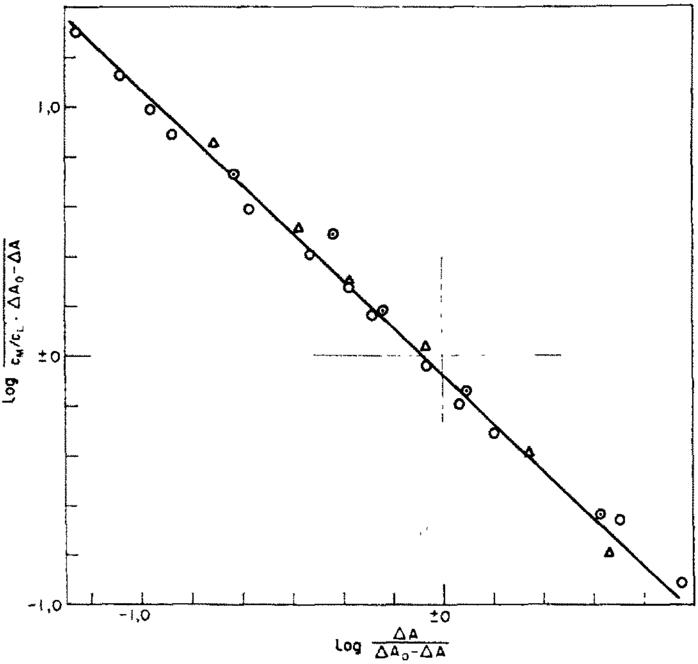


Abb. 8.—Transformierte photometrische Titrationskurven.
○ $c_L = 2 \cdot 10^{-5} M$; △ $c_L = 5 \cdot 10^{-5} M$; ⊙ $c_L = 1 \cdot 10^{-4} M$.

auf 5,0 · 10^4 bei 642 nm. Mit Rücksicht auf den bekannten Wert[2] von $\varepsilon_{L,642}$ = 1,45 · 10^4, folgt für den maximalen Wert von ε_{ML} 6,45 · 10^4. Da in dem untersuchten pH-Gebiet 1,7–3,7 ε_L praktisch konstant bleibt und die Lage des Absorptionsmaximum sich nicht ändert, bleibt auch $\Delta\varepsilon_{ML}$ in diesem pH-Gebiet konstant. Die ermittelten Werte von K und $\Delta\varepsilon_{ML}$ liegen in sehr guter Übereinstimmung mit den experimentellen Angaben, die bei der Aufstellung der Jobschen Kurve gewonnen wurden. Die ausgezogene Kurve in Abb. 6 wurde aus K und $\Delta\varepsilon_{ML}$ errechnet.

Auch die mit Hilfe von $\Delta\varepsilon_{ML} = 5 \cdot 10^4$ aus $\Delta\varepsilon_{ML,\text{eff}}$ bei konstanten Verhältnissen c_L/c_M, Abb. 4, errechneten K-Werte stimmten sowohl bei pH 2,80 als auch bei pH 2,30 mit der auf Abb. 3 dargestellten Abhängigkeit überein.

Der relativ niedrige K-Wert bewirkt die merkliche Abhängigkeit der Richtungskoeffizienten der linear ansteigenden Teile der photometrischen Titrationskurven, wobei handelt es sich eigentlich um die Eichkurven für die spektralphotometrische Anwendung von Sulfonazo III zurBariumbestimmung (vgl. Abb. 5). DieseErscheinung kann zur gleichzeitigen Bestimmung von K und $\Delta\varepsilon_{ML}$ aus den Messungen im Gebiet eines Überschusses an Komplexbildner, also bei Bedingungen der analytischen Anwendung des Reagenzes herangezogen werden, siehe Theoretischen Teil.

Die Gültigkeit der abgeleiteten Beziehung für die bei der Aufstellung von photometrischen Titrationskurven gewonnenen Angaben (pH 2,80, Essigsäure und pH 1,9, Britton–Robinsonscher Puffer) ist aus der Abb. 9 ersichtlich. Der extrapolierte K-Wert betrug 4,2 · 10^4 bei pH 2,80 und 1,3 · 10^4 bei pH 1,9. Die Richtungskoeffizienten beider Geraden (Abb. 9) geben den Wert von $\Delta\varepsilon_{ML} = (4{,}8 \pm 0{,}3) \cdot 10^4$ an. Diese Werte stehen in guter Übereinstimmung mit jenen, die bei der Auswertung ganzer

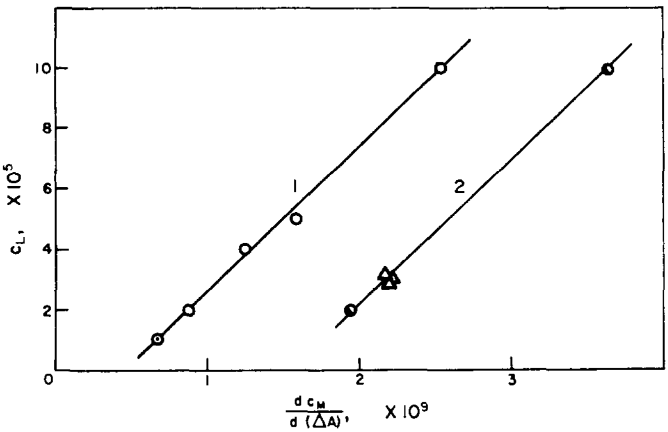


ABB. 9.—Abhängigkeit der Richtungskoeffizienten der Eichkurven von c_L. *1*—pH 2,80 Essigsäure; *2*—pH 1,9 Britton-Robinson. ⊙ aus $\Delta\varepsilon_{ML,eff}$, Abb. 6, $\Delta_{3,2}$, $\Delta_{4,5}$, errechneten Werte; Δ Analysen der Handelsprodukte.

Titrationskurven, bzw. bei der Untersuchung des pH-Einflusses auf die Komplexbildung, erhalten wurden.

Diese Ergebnisse deuten auf breitere Anwendungsmöglichkeiten der Beziehung (10) hin, z.B. in Fällen bei welchen die extrapolative Bestimmung von $\Delta\varepsilon_{ML}$ bei Bedingungen eines großen Überschusses an c_M nicht möglich ist (u.a. Bildung eines anderen Komplexes).

Um die Gültigkeit der gewonnenen Werte und Beziehungen auch für die handelsüblichen Natriumsalze von Sulfonazo III zu überprüfen, untersuchten wir den Einfluß von Natriumionen auf die Bildung des Bariumkomplexes, und auch die Störungen durch Calciumionen die mit Sulfonazo III gleichfalls blau gefärbte Komplexe liefern.

Nach den Angaben in Abb. 7 macht sich die Anwesenheit von Natrium bei den Bedingungen der photometrischen Bariumbestimmung (Überschuß an Sulfonazo III) bei niedrigeren Konzentrationen als etwa $5 \cdot 10^{-3}M$ nicht bemerkbar. Bei einem Bariumüberschuß, d.h. praktisch bei der Anwendung von Sulfonazo III als Indicator, wirken sich bei pH 2,80 etwa $5 \cdot 10^{-2}M$ Natriumkonzentrationen störend aus.

Calciumionen stören die Bestimmung bei Konzentrationen $> 5 \cdot 10^{-4}M$. Die bei kleinen Natrium- und Calciumkonzentrationen bestimmten Werte von $\Delta\varepsilon_{ML,eff}$ stimmen gut mit den auf der Abb. 4 bzw. 9 dargestellten Abhängigkeiten und somit auch mit den an der reinen Säure gewonnenen Werten von K und $\Delta\varepsilon_{ML}$ überein. In guter Übereinstimmung mit dem Verhalten der reinen Säure stehen auch die von dem Betriebslaboratorium bei pH 1,9 (Britton-Robinsonscher Puffer) auf dem Spektralphotometer VSU-1 (C. Zeiss, Jena) bei den Kontrollanalysen gemessenen Werte der Richtungskoeffizienten der Handelspräparate Sulfonazo III, *p.a.*, Lachema Brno. Ergebnisse dieser Messungen sind gleichfalls in Abb. 9 dargestellt.

Abweichende und ausserdem nicht reproduzierbare Ergebnisse bekamen wir bei Verwendung von an der H^+-Form von Dowex-50 entsalzenen Lösungen reiner Natriumsalze von Sulfonazo III, ohne nachträglicher Umfällung. Nach Umfällung der entsalzenen Lösungen mit Säure[2] wurden diese Schwierigkeiten nicht mehr beobachtet.

Es ist notwendig, die Bedingungen bei der Anwendung von Sulfonazo III für die photometrische Bariumbestimmung streng zu standardisieren. Bei Einhaltung konstanter Bedingungen ist es dann möglich auch die hohen Werte von $\Delta\varepsilon_{\mathrm{ML,eff}}$ bei höheren Sulfonazo III-Konzentrationen auszunutzen: Bei pH 2,80 kann z.B. Barium in einer Konzentration von $2 \cdot 10^{-6}M$ bei $c_L = 1 \cdot 10^{-4}M$, $\Delta\varepsilon_{\mathrm{ML,eff}} = 4{,}0 \cdot 10^4$, mit einem Fehler von ± 5% (Variationskoeffizient von 10 Bestimmungen) bestimmt werden.

Summary—Barium forms a 1:1 complex with Sulphonazo III in the pH range 1·9–2·8, with $\varepsilon = 6{\cdot}45 \times 10^4$ at 642 mμ. In the practical determination of barium by the proposed method, the effective value of ε ranges from 1·5–4·0 × 10^4, depending on pH and total reagent concentration, due to dissociation of the weak complex. Using a new method for the determination of the extinction coefficients of weak complexes, the values for this system, and also the apparent formation constants, have been found, and the composition of the complex verified for the pH range 1·7–3·3.

Résumé—Le baryum forme un complexe 1 : 1 avec le Sulfonazo III dans le domaine de pH 1,9–2,8, avec $\varepsilon = 6{,}45 \times 10^4$ à 642 mμ. Dans le dosage pratique du baryum par la méthode proposée, la valeur réelle de ε varie de 1,5 à 4,0 × 10^4, en fonction du pH et de la concentration totale en réactif, ce qui est dû à la dissociation du complexe faible. En utilisant une nouvelle méthode pour la détermination des coefficients d'extinction de complexes faibles, on a trouvé les données pour ce système et aussi les constantes de formation apparentes, et vérifié la composition du complexe dans le domaine de pH 1,7–3,3.

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RAPID SPECTROPHOTOMETRIC DETERMINATION OF COBALT WITH 2,2′-DIPYRIDYL KETOXIME

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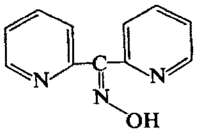
Summary—A rapid spectrophotometric method for the determination of low levels of cobalt(III) with 2,2 -dipyridyl ketoxime is proposed. A 3:1 water-soluble complex which is easily extractable into chloroform and has an absorption maximum at 388 mμ forms instantaneously. Beer's law is obeyed and the molar absorptivity is $19{\cdot}5 \times 10^3$. An investigation of the interference of 60 cations and anions shows the method to be widely applicable; it is simple, convenient and reproducible.

NUMEROUS spectrophotometric methods have been proposed for the determination of cobalt.[1–4] Of these, the nitroso-R-salt method is well established for the determination of traces of cobalt in such substances as soils, plants, animal organs and metallurgical products.[3] More recently, phenanthrenequinone monoxime[5] and 2-thenoyltrifluoroacetone[6] have been proposed for the spectrophotometric determination of cobalt, and dithio-oxamide[7] and 2,3-quinoxalinedithiol[8] have both been proposed for the simultaneous determination of cobalt and another metal. The last-named reagent is claimed to be one of the most sensitive for cobalt.

2,2′-Dipyridyl ketoxime (I) which has been reported as a new reagent for the spectrophotometric determination of gold[9] and palladium[10] is also suitable for the determination of cobalt. It reacts instantaneously in a basic citrate medium to form a water-soluble chelate which is easily extractable into chloroform. The method is highly sensitive, and relatively free from interferences.



(I)

The reagent has the advantages that its ethanolic solution is stable indefinitely, and that symmetry precludes *syn*- and *anti*-isomers. Furthermore, the ketone is commercially available and to make the oxime takes only 5 min of refluxing with hydroxylamine hydrochloride.

EXPERIMENTAL

Reagents

2,2′-Dipyridyl ketoxime. The parent ketone was either prepared[9,11] or purchased (Aldrich) and converted directly[12] with hydroxylamine hydrochloride into the oxime, which was used as a 1% solution in 95% ethanol. The solution is colourless and indefinitely stable towards light.

Standard cobalt solution. Ultra-pure cobalt metal was dissolved in *aqua regia*, and the solution was evaporated nearly to dryness, diluted to 1 litre with doubly-distilled water, and further diluted to give a standard solution containing 8·86 mg of cobalt/ml. Class A glassware was used.

Other chemicals. Reagent grade chlorides or nitrates were used to make solutions of diverse cations, and potassium or sodium salts for the anion solutions. ACS grade chloroform was used without further purification.

Procedure

Dissolve the sample by appropriate means and place an aliquot containing 6–60 μg of cobalt in a 60-ml separating funnel with a small plug of pyrex glass wool in the stem. Add about 3 ml of 50% sodium citrate solution and 1 drop of phenolphthalein indicator and adjust the pH with dilute potassium hydroxide or hydrochloric acid until a distinct pink colour appears. Dilute the contents to 15–20 ml with distilled water, add 3 ml of reagent solution, and shake the contents briefly. Extract twice with 7–8 ml portions of chloroform, transferring the extracts into a 25-ml glass-stoppered graduated cylinder. The glass-wool plug removes traces of water. Dilute the combined extracts to volume with solvent. Prepare a blank similarly. Measure the absorbance of the extract at 388 mμ and read off the amount of cobalt from a previously prepared calibration curve.

RESULTS AND DISCUSSION

Spectral characteristics

The chloroform solution of the complex exhibits an absorption maximum at 388 mμ and at this wavelength there is negligible absorption due to the reagent (Fig. 1). Beer's law is obeyed up to 3·5 ppm of cobalt; the molar absorptivity at 388 mμ is $19{\cdot}5 \times 10^3$ and the Sandell sensitivity[13] is 0·0029 $\mu g.cm^{-2}$.

Iron(II), copper(I) and copper(II) also form highly coloured complexes with the reagent.

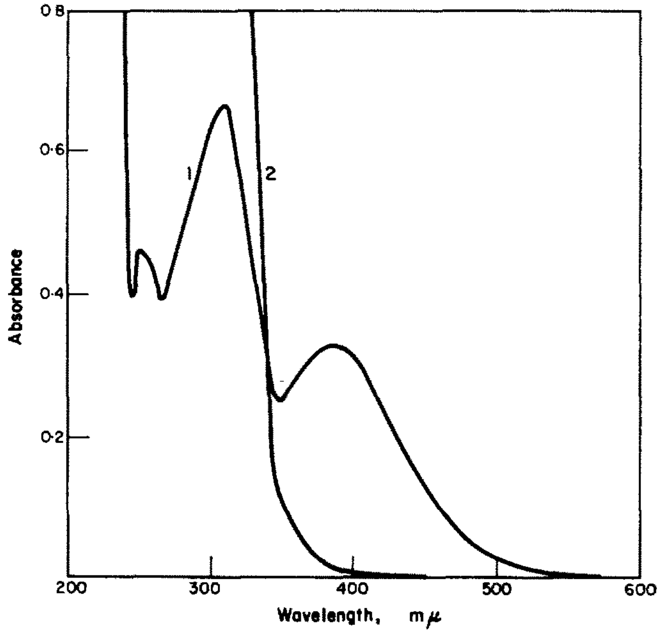


FIG. 1.—Absorption spectra of cobalt(III) chelate and reagent.
1. Pure Co(III) chelate [1·06 ppm Co(III)] in chloroform.
2. Reagent in ethanol.

Effect of pH

The optimum pH range for chelate formation and extraction was found to be 8·0–9·5 as the following values of absorbance at various pH (in brackets) show: 0·212 (11·9), 0·255 (11·0), 0·317 (9·8), 0·321 (9·6), 0·324 (8·7), 0·322 (8·2), 0·318 (7·8), 0·313

(7·1) and 0·059 (5·1). Reaction was instantaneous and no cobalt could be detected by dithio-oxamide in the aqueous layer after extraction for 30 sec with 10 ml of chloroform. The completeness of extraction was confirmed by the constant absorbance of the second and third chloroform extracts.

Effect of time, reagent concentration and temperature

The absorbances of chloroform extracts of the complex extracted immediately the complex had been formed, and 10 hr after formation, were identical. The absorbance of the extract was constant for 3 days but decreased by approximately 6% during two weeks. There was no change in absorbance when 3 ml or 6 ml of the reagent were added. Normal variations in room temperature did not affect the absorbance.

Choice of solvent

The chelate can be extracted completely by chloroform or dichloromethane, partially by n-amyl alcohol, benzene, ethyl acetate, nitrobenzene or toluene, but not at all by carbon tetrachloride, cyclohexane, diethyl ether, hexane, or xylene. Chloroform was preferred to dichloromethane because of its lower volatility and higher specific gravity. The insolubility in carbon tetrachloride is noteworthy.

Precision and accuracy

The precision and accuracy of the method were studied by analysing (10 times) solutions containing known amounts of cobalt. The results are summarized in Table I.

TABLE I.—PRECISION AND ACCURACY

Cobalt, *ppm*		Rel. std. dev., %	Range, *ppm*
Taken	Found		
0·35	0·35	1·2	0·01
1·06	1·06	0·19	0·00
2·13	2·12	0·48	0·03

Effect of diverse ions

To study the effect of interferences a 200-fold excess of a foreign ion was added to 26·58 μg of cobalt and the determination performed. The following ions did not interfere at this level: Ca(II), Ba(II), Al(III), $Cr_2O_7^{2-}$, Pt(II), Ru(III), Br^-, F^-, I^-, Cl^-, UO_2(VI), Zr(IV), V(IV), V(V), WO_4^{2-}, Se(IV), Sn(II), Sn(IV), Hf(IV), In(III), Cr(III), Mo(VI), Th(IV), Ga(III), $S_2O_4^{2-}$, NO_3^-, SO_4^{2-}, Na(I), K(I), Bi(III), Sr(II), Tl(I), Re(VII), Nb(V), Ta(V) and Ti(IV). One mg of Mg(II) or Cd(II), and 4 mg of Te(IV), could be tolerated and so could large amounts of ClO_4^-, $S_2O_8^{2-}$, NO^{2-}, $S_2O_3^{2-}$ and $C_2O_4^{2-}$.

Five mg of the following ions can be masked by addition of 2 ml of 5% sodium pyrophosphate solution: Zn(II), Be(II), Pb(II), As(III), Sb(V), Fe(III); 1 mg of Mn(II) and Rh(III) were also masked under these conditions. Five mg of Ag(I), Au(III), or Hg(II) can be masked with 2 ml of 5% sodium thiosulphate solution, and 5 mg of Ir(III) with 1 ml of 10% thiourea solution.

Interference due to nickel was removed by washing the organic extract with 12–15 drops of concentrated hydrochloric acid, which decomposed the nickel chelate but not the cobalt chelate.

Palladium and copper were separated by prior extraction of their acetylacetonates with 10 ml of 1:1 v/v mixture of acetylacetone and chloroform at pH ~2. Then 3 ml of 50% sodium citrate solution were added and the procedure followed.

EDTA and cyanide interfere severely and must be absent. The presence of ammonium salts is also objectionable in alkaline media because they interfere by amine formation.

Composition, stability, and structure of the complex

The composition of the soluble cobalt complex was found by the mole-ratio method[14] to be 3:1 reagent:cobalt (Fig. 2).

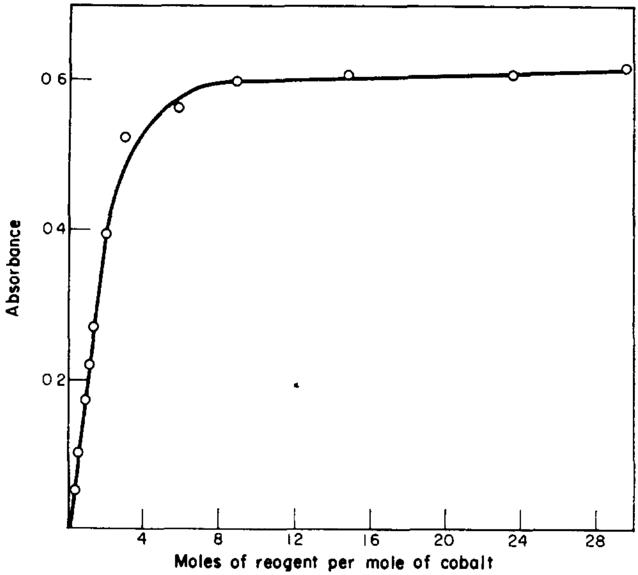


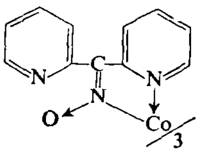
FIG. 2.—Mole-ratio plot.
Cobalt(III) 3·2 × $10^{-5}M$ with varying concentrations of ligand.

This was confirmed by analysis of the orange solid left by evaporation of the chloroform extract: found C, 60·5%; H, 3·9%; N, 19·2%; Co, 9·0%: $Co(C_{11}H_8N_3O)_3$ requires C, 60·65%; H, 3·70%; N, 19·29%; Co, 9·02%. When the isolated solid complex was dissolved in chloroform, a spectrum identical with that of the extracted species was obtained.

That cobalt exists in the tervalent state in the complex is supported by its stability in strongly acidic solutions, a characteristic of spin-paired d^6 cobalt complexes.[15]

The dissociation constant of the complex[16] may be written as $K = \alpha c(n\alpha c)^n/c(1 - \alpha)$ where $n = 3$, c is the molarity of the solution of the complex and α is the degree of dissociation defined by $\alpha = (A_M - A_S)/A_M$. The values of α and c are obtained directly from Fig. 2. A_M is the maximum absorbance obtained from the horizontal portion of the curve and A_S is the absorbance at the stoichiometric molar ratio of reagent to cobalt in the complex. The experimental value of K is 7·09 × 10^{-16}. Reliable values of K are generally obtained when A_S/A_M is between 0·7 and 0·9;[17] in the present work, the value was 0·84.

The chelate may be represented by:



(II)

Preliminary spectroscopic evidence indicates bonding through the nitrogen of the oxime group rather than through the oxygen of the hydroxyl group. This type of linkage was indicated in the infrared spectrum by the frequency shift of the C=N vibration. In the pure oxime this vibration was assigned to the peak at 1550 cm^{-1}.[10] In the protonated perchlorate complex of 2,2′-dipyridyl ketoxime, the C=N frequency shifts to 1530 cm^{-1}. The effect of proton removal [structure (II)] shifts the C=N frequency to 1489 cm^{-1}. This trend is in agreement with that found by previous workers[18] who investigated pyridine-2-formaldoxime, a closely related compound.

Acknowledgement—This work was supported by a grant from the National Research Council of Canada and a Province of Ontario Fellowship.

Zusammenfassung—Eine schnelle spektrophotometrische Methode zur Bestimmung kleiner Kobalt(III)-Konzentrationen mit 2,2′-Dipyridylket-oxim wird vorgeschlagen. Es bildet sich augenblicklich ein wasser-löslicher 3:1-Komplex, der sich leicht in Chloroform extrahieren läßt und ein Absorptionsmaximum bei 388 nm hat. Das Beersche Gesetz gilt, der Extinktionskoeffizient ist 19,5 · 10^3. Eine Untersuchung über die Storungen von 60 Kationen und Anionen zeigt die weite Anwendbarkeit der Methode; sie ist einfach, bequem und reproduzierbar.

Résumé—On propose une méthode spectrophotométrique rapide pour le dosage de faibles teneurs de cobalt (III) par la 2,2′-dipyridyl cétoxime. Il se forme instantanément un complexe 3:1 soluble dans l'eau, aisément extractible en chloroforme et qui a un maximum d'absorption à 388 nm. La loi de Beer est suivie et le coefficient d'absorption moléculaire est de 19,5 × 10^3. Une recherche sur l'interférence de 60 cations et anions montre que la méthode est largement applicable; elle est simple, commode et reproductible.

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SHORT COMMUNICATIONS

Stability constants of some metal complexes of triethylenetetraminehexa-acetic acid and complexometric titration of rare earths and other metals

(*Received* 27 *February* 1968. *Accepted* 10 *March* 1968)

TRIETHYLENETETRAMINEHEXA-ACETIC ACID (TTHA) has been shown to be an interesting complexing agent. Sievers and Bailar[1] studied the infrared spectra of its metal complexes and Bohigian and Martell[2] reported the stability constants of its complexes with magnesium, calcium, copper, cobalt, nickel, lanthanum, and thorium. Přibil and Veselý[3] reported its use as a titrant in determining many metals.

We have determined potentiometrically the stability constants of some metal complexes of TTHA by using a similar method to that reported by Bohigian and Martell.[2] The results for the non-protonated TTHA complexes are shown in Table I. Those for the protonated TTHA complexes and the 2:1 non-protonated complexes will be reported soon. Our results agree well with those reported by Bohigian and Martell. For instance, they reported log *K* for the La–TTHA (1:1) complex as 23·1 and we found log *K* for the Sm–TTHA (1:1) complex to be 24·3.

TABLE I.—STABILITY CONSTANTS OF SOME NON-PROTONATED 1:1 METAL COMPLEXES OF TTHA

Metal	log *K*	
	This work	Bohigian and Martell[2]
Cadmium	19·8	—
Cobalt	20·4	20·6
Nickel	19·9	18·8
Lead	19·5	—
Samarium(III)	24·3	—
Zinc	20·1	—

The stability constants for most rare earth TTHA complexes have not yet been determined, but we have titrated all the rare earth metals, except promethium, with TTHA and found that they form 1:1 complexes under the titration conditions. A back-titration method was used, in which a slight excess of TTHA was added, the pH was adjusted to 6·0–6·2 with solid hexamine, and the excess of TTHA was titrated with standard lanthanum solution, Methylthymol Blue being used as indicator. For 0·5 mmole of the rare earth, the average error was 0·5%. As reported previously, cerium(IV) is hydrolysed in slightly acidic medium even in the presence of EDTA and DTPA. It was found that cerium(IV) was also hydrolysed in the presence of TTHA at pH 2–6. On heating, the cerium precipitate gradually dissolved, through stages showing brown and yellow colours, until finally the solution became colourless. Cerium(IV) is easily reduced by ascorbic acid and then conveniently titrated with TTHA. For less than 1 mmole of rare earth metal, it is possible to titrate direct with TTHA at pH 5–6, but we prefer the back-titration technique.

We found both zirconium and hafnium were hydrolysed in the presence of TTHA at pH 1, but could be complexed by excess of TTHA if the solution was heated for 10 min at 90°; after cooling, the excess of TTHA could be back-titrated with either lanthanum or lead at pH 6·2, with Methylthymol Blue as indicator. Other metals not previously studied with TTHA are under investigation.

Acknowledgements—The authors express their appreciation to T. A. Bohigian for his assistance in computing the stability constants and to Terry Jones for his assistance in performing the rare earth titrations.

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Summary—The stability constants of some non-protonated 1:1 metal complexes of triethylenetetraminehexa-acetic acid are reported; log K values are Cd 19·8, Co(II) 20·4, Ni 19·9, Pb 19·5, Sm(III) 24·3, Zn 20·1.

Zusammenfassung—Die Stabilitätskonstanten einiger nichtprotonierter Metallkomplexe (1:1) von Triäthylentetraminhexaessigsäure werden mitgeteilt; die log K-Werte sind für Cd 19,8; Co (II) 20,4; Ni 19,9; Pb 19,5; Sm (III) 24,3; Zn 20,1.

Résumé—On rapporte les constantes de stabilité de quelques complexes métalliques non protonés 1:1 de l'acide triéthylènetétraminehexa-acétique; les valeurs de log K sont Cd 19,8; Co(II) 20,4; Ni 19,9; Pb 19,5; Sm(III) 24,3; Zn 20,1.

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Improved specific separation of selenium by solvent extraction with saturated monoketones

(*Received* 22 *December* 1967. *Accepted* 18 *March* 1968)

In previous papers[1-4] we have shown that in moderately concentrated hydrochloric acid, selenium(IV) reacts with saturated aliphatic monoketones (acetone, ethyl methyl ketone, diethyl ketone, isobutyl methyl ketone, *etc.*) to form organoselenium compounds that are soluble in chloroform. In our earlier work we were unable to decide which was the most suitable ketone, or the best method for complete decomposition of organoselenium compounds without loss of selenium. The aim of the present paper is to deal with these problems.

EXPERIMENTAL

The experiments were carried out with a solution containing 100 μg of selenium per ml and labelled with the β-active isotope ^{75}Se; 1 ml of this solution had an activity of 4670 cpm. The ketones used were distilled, and then stored in the dark. The hydrochloric acid must contain no free chlorine, because the latter interferes with formation of the organoselenium compounds.

Choice of ketones

According to our previous work,[4] the rates of interaction of selenium with various ketones do not differ significantly (except for isobutyl methyl ketone), at the same acidity. In the present investigation, attention was given to the availability of the ketones and to their behaviour during the decomposition of the organoselenium compound. The most suitable were acetone, ethyl methyl ketone and acetophenone.

Investigation of extractability

The aqueous phase containing 100 μg of selenium and 0·025–1·0 ml of ketone was acidified to the desired degree, diluted to 10 ml and shaken. After standing for 30 min, the organoselenium compound was extracted with 10 ml of chloroform, and the activity of both phases was measured. Formation of the organoselenium compound begins at lower acidity with acetone or ethyl methyl ketone than with acetophenone, but at sufficiently high acidity formation is most complete with acetophenone.

Financial support by the school of graduate studies University of Missouri — Kansas City is gratefully acknowledged.

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Summary—The stability constants of some non-protonated 1:1 metal complexes of triethylenetetraminehexa-acetic acid are reported; log *K* values are Cd 19·8, Co(II) 20·4, Ni 19·9, Pb 19·5, Sm(III) 24·3, Zn 20·1.

Zusammenfassung—Die Stabilitätskonstanten einiger nichtprotonierter Metallkomplexe (1:1) von Triäthylentetraminhexaessigsäure werden mitgeteilt; die log *K*-Werte sind für Cd 19,8; Co (II) 20,4; Ni 19,9; Pb 19,5; Sm (III) 24,3; Zn 20,1.

Résumé—On rapporte les constantes de stabilité de quelques complexes métalliques non protonés 1:1 de l'acide triéthylènetétraminehexa-acétique; les valeurs de log *K* sont Cd 19,8; Co(II) 20,4; Ni 19,9; Pb 19,5; Sm(III) 24,3; Zn 20,1.

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Improved specific separation of selenium by solvent extraction with saturated monoketones

(*Received* 22 *December* 1967. *Accepted* 18 *March* 1968)

IN PREVIOUS papers[1–4] we have shown that in moderately concentrated hydrochloric acid, selenium(IV) reacts with saturated aliphatic monoketones (acetone, ethyl methyl ketone, diethyl ketone, isobutyl methyl ketone, *etc.*) to form organoselenium compounds that are soluble in chloroform. In our earlier work we were unable to decide which was the most suitable ketone, or the best method for complete decomposition of organoselenium compounds without loss of selenium. The aim of the present paper is to deal with these problems.

EXPERIMENTAL

The experiments were carried out with a solution containing 100 μg of selenium per ml and labelled with the β-active isotope ^{75}Se; 1 ml of this solution had an activity of 4670 cpm. The ketones used were distilled, and then stored in the dark. The hydrochloric acid must contain no free chlorine, because the latter interferes with formation of the organoselenium compounds.

Choice of ketones

According to our previous work,[4] the rates of interaction of selenium with various ketones do not differ significantly (except for isobutyl methyl ketone), at the same acidity. In the present investigation, attention was given to the availability of the ketones and to their behaviour during the decomposition of the organoselenium compound. The most suitable were acetone, ethyl methyl ketone and acetophenone.

Investigation of extractability

The aqueous phase containing 100 μg of selenium and 0·025–1·0 ml of ketone was acidified to the desired degree, diluted to 10 ml and shaken. After standing for 30 min, the organoselenium compound was extracted with 10 ml of chloroform, and the activity of both phases was measured. Formation of the organoselenium compound begins at lower acidity with acetone or ethyl methyl ketone than with acetophenone, but at sufficiently high acidity formation is most complete with acetophenone.

Moreover, the extractability is independent of the total ethyl methyl ketone or acetophenone concentration whereas it is strongly dependent on acetone concentration. The influence of sulphuric acid was examined because some types of sample are dissolved in sulphuric acid; sulphuric acid up to $2M$ concentration does not affect the extraction.

Decomposition of the organoselenium compound

It is very difficult to decompose the organoselenium compound completely without formation of coloured decomposition products and loss of selenium. Many possibilities were studied. The best found was the one used in the recommended procedure. Its efficiency was checked radiometrically and no loss of selenium was found.

Composition of the acetophenone–selenium compound

Selenium dioxide was dissolved in $7M$ hydrochloric acid in a separatory-funnel, then acetophenone (mole ratio acetophenone:selenium = 2·5) was added dropwise with shaking. After formation of a white crystalline precipitate the mixture was shaken vigorously for a long time and allowed to stand for 2 hr. Excess of ketone was extracted into benzene and the precipitate was filtered off under suction, washed first with chloroform, then with ethanol, and dried at room temperature. The white needle-shaped crystals were soluble in acetophenone and chloroform. Elementary analysis corresponded to the formula $SeCl_2(C_8HO_7)_2$.

APPLICATIONS

Determination of selenium in copper concentrate

Add 15 ml of conc. hydrochloric acid to 0·2–2 g of sample (depending on the selenium content). Heat on a water-bath until the evolution of hydrogen sulphide ceases, cool slightly and add 5 ml of conc. nitric acid; heat on a sand-bath at 200° and evaporate to a moist residue; dissolve the latter in 3–4 ml of conc. hydrochloric acid and evaporate again, repeating this twice more to remove the nitric acid and to dehydrate the silicic acid. Do not evaporate to dryness or heat the residue for long, lest selenium should partially volatilize. Filter off the silicic acid on a medium porosity filter and wash it with 7–8 M hydrochloric acid. Collect the filtrate in a 50-ml volumetric flask and dilute to volume with the same acid. Place 10 or 20 ml of the solution in a separatory-funnel, add 0·015 ml of acetophenone, shake the mixture, let it stand for 30 min. and extract first with 10 ml and then 5 ml of chloroform (3-min shaking). Combine the extracts in another separatory-funnel and wash with 3 ml of water for 30 sec. Transfer the extract to a 25-ml volumetric flask and evaporate the chloroform on a boiling water-bath. Add 1 ml of conc. sulphuric acid and 3–4 drops of conc. nitric acid to the dry residue and heat for 20–30 min on a sand-bath at 200°. Cool the solution, add 1 ml of water and heat again to remove nitric acid and oxides of nitrogen, repeating this if the solution is not completely colourless. Dilute with water, cool to room temperature, and add 1 ml of 0·5% gelatine solution, 1 ml of conc. hydrochloric acid, 0·5 ml of 1% bismuth nitrate solution and 1 ml of 25% tin(II) chloride solution. Shake the mixture, dilute to the mark, let stand at 20° for 40 min, and measure the absorbance at 430 mμ against a reagent blank, in 5-cm cells. Prepare a calibration curve covering the range 5–25 μg of selenium.

When the method was applied to a copper concentrate the selenium content was found to be 91 ppm, standard deviation 3 ppm (10 results). Standard addition experiments showed complete recovery of selenium.

Determination of selenium in tellurium

Dissolve 1–5 g of tellurium (depending on the selenium content) in 10 ml of *aqua regia*, on a sand-bath, and evaporate almost to dryness. Take up the moist residue in 10 ml of $8M$ hydrochloric acid, add 0·5 g of urea and evaporate again. Take up the residue in $8M$ hydrochloric acid and transfer the solution to a 50-ml volumetric flask. Add 0·015 ml of acetophenone to an aliquot of this solution, and after 30 min extract with 15 ml of chloroform. Wash the organic phase with 4 ml of water, shaking for 30 sec, filter through a paper moistened with chloroform, and determine the selenium as for copper concentrates. This method gives the possibility of determining selenium in tellurium of high purity (99·9–99·999%).

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Summary—Acetophenone is the most suitable ketone for extraction of selenium into chloroform. Methods are given for determination of selenium in copper concentrates and metallic tellurium.

Résumé—L'acétophénone est la cétone la plus appropriée pour l'extraction du sélénium en chloroforme. On donne des méthodes pour le dosage du sélénium dans des concentrats de cuivre et dans le tellurium métallique

Zusammenfassung—Zur Extraktion von Selen in Chloroform ist Aceto-phenon das geeignetste Keton. Es werden Vorschriften zur Selenbestimmung in Kupferkonzentraten und in metallischem Tellur angegeben.

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2. *Idem*, *ibid.*, 1966, **13**, 163.
3. L. Futekov and N. Jordanov, *ibid.*, 1966, **13**, 763.
4. N. Jordanov and L. Futekov, *Izv. Inst. po Obshcha Neorg. Khim. Bulgar. Akad. Nauk*, 1966, **4**, 25.

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New chromogens of the ferroin-type—II

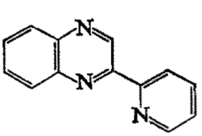
Pyrido and pyridyl derivatives of phenazine and quinoxaline

(*Received* 25 *January* 1968. *Accepted* 2 *March* 1968)

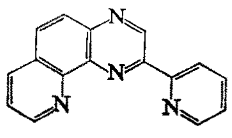
In CONNECTION with further studies in the preparation of sensitive and selective chromogens of the ferroin type,[1] Pfeiffer and Case[2] recently synthesized a variety of phenazine and quinoxaline derivatives. The quinoxaline derivatives have in common a 2-pyridyl group, and the phenazines a pyrido[2,3-*a*] group. Since the donor-atom groups of the former have greater flexibility than those of the latter, a comparative study of the chromogenic properties of the two types is of interest. It should reveal which is more conducive to chelation, flexibility or rigidity. Also, certain of the new derivatives possess two ferroin-type groups, each free to act independently of the other. The possibility that these compounds might form chelation polymers with metal ions also merits investigation. Hence, a study of the reactions of the new compounds with iron(II) and copper(I) has been made. The compounds are identified below by name and structure. They will be referred to by the roman numeral assigned to each.

Quinoxaline derivatives

2-(2-Pyridyl)quinoxaline (I)



2-(2-Pyridyl)pyrido[3,2-*h*]quinoxaline (II)



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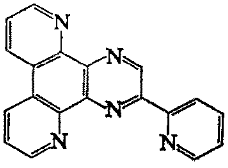
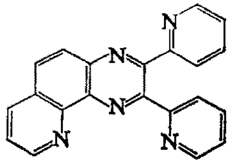


2,3-bis(2-Pyridyl)pyrido[2,3-*f*]quinoxaline (IV)



Summary—Acetophenone is the most suitable ketone for extraction of selenium into chloroform. Methods are given for determination of selenium in copper concentrates and metallic tellurium.

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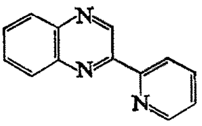
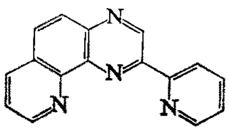
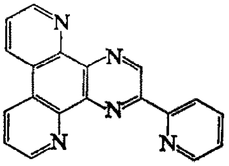


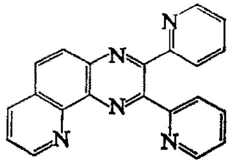
2-(2-Pyridyl)pyrido[3,2-*h*]quinoxaline (II)



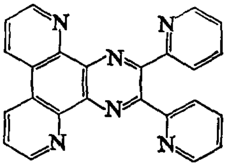
2-(2-Pyridyl)dipyrido[2,3-*f*:3′,2′-*h*]quinoxaline (III)



2,3-bis(2-Pyridyl)pyrido[2,3-*f*]quinoxaline (IV)

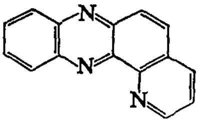


2,6-bis(2-Pyridyl)dipyrido[2,3-*f*:3′,2′-*h*]quinoxaline (V)

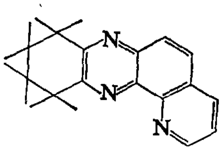


Phenazine derivatives

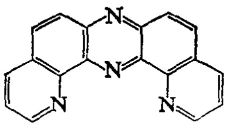
Pyrido[2,3-*a*]phenazine (VI)



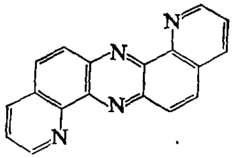
8,9,10,11-Tetrahydropyrido[2,3-*a*]phenazine (VII)



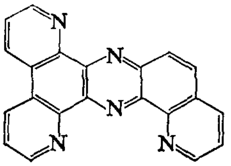
Dipyrido[2,3-*a*:3′,2′-*j*]phenazine (VIII)



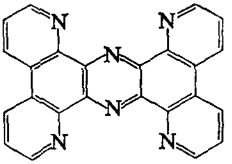
Dipyrido[2,3-*a*:2′,3′-*h*]phenazine (IX)



Tripyrido[2,3-*a*:3′,2′-*c*:3″,2″]-*j*-phenazine (X)



Tetrapyrido[2,3-*a*:3′,2′-*c*:2″,3″-*h*:3‴,2‴-*j*]phenazine (XI)



EXPERIMENTAL

Samples of the eleven new chromogens investigated were provided by Dr. Francis H. Case of Temple University. The small amount of compound II available permitted study of only the iron(II) reaction. Analytical and preparative details have been reported elsewhere.[3]

A description of the various standard solutions, pH buffers, reagents, and procedures used in this investigation appears in the previous publication of this series.[1] A 5-cm cell was used for spectral measurements of the very weakly absorbing iron(II) chelates of compounds I, VI and VII.

RESULTS AND DISCUSSION

Some properties of the iron(II) and copper(I) chelates of the new chromogens are listed in Table I. Marked differences exist between the iron(II) chelates of the quinoxaline derivatives and those of the phenazine derivatives. The iron(II) chelates of the quinoxaline derivatives exhibit greater absorptivities and shorter wavelengths of absorbance maxima than those of the more rigid phenazine derivatives. The effect of ligand flexibility is particularly striking on comparing the following closely related pairs: II and VIII, III and X, IV and X, V and XI. Each of the six compounds should act as a terdentate ligand with respect to iron(II) co-ordination. The spectral data clearly reveal that a certain degree of flexibility must be present in a terpyridine-type ligand if it is to be a sensitive iron chromogen. Two of the nitrogen donor atoms may be in a rigid fused ring system, as exemplified by 1,10-phenanthroline, but the third nitrogen donor atom must be incorporated in a flexible portion of the ligand, such as a pyridyl (but not a pyrido) group. Additional examples of this empirical rule can be cited. The flexible terdentate ligands 2,2′,2″-terpyridine and 2,3,5,6-tetra-2-pyridylpyrazine are closely related to compounds VIII and XI, respectively. Both form intensely coloured iron(II) chelates,[3,4] but the more rigid compounds VIII and X do not. Flexibility thus plays an important role in determining the spectral characteristics of the iron(II) chelates of these terdentate ligands. The nature of this role is not known. It could be steric, electronic, or both.

TABLE I.—PROPERTIES OF THE METAL CHELATES

Metal ion	Chromogen	Chelate colour	pH range for max. colour	Extractability	λ *nm*	ε
Fe(II)	I	pale red	4–9	nil	538	30
	II	purple	4–8	nil	594	9500
	III	purple	4–9	nil	579	18700
	IV	purple	4–8	nil	592	18300
	V	purple	4–9	nil	589	21800
	VI	pale green	4–9	nil	660	110
	VII	pale red	4–10	nil	478	145
	VIII	pale green	4–8	nil	725	520
	IX	green (ppte.)	2–11	nil	—	—
	X	pale green	4–9	nil	719	710
	XI	green (ppte.)	2–11	nil	—	—
Cu(I)	I	purple	3–9	complete	525	4600
	II	—	—	—	—	—
	III	orange	5–9	nil	482	5000
	IV	orange	5–8	complete	484	3900
	V	orange	5–8	complete	490	4400
	VI	violet	3–9	complete	550	6800
	VII	gold	3–9	complete	470	7700
	VIII	blue ppte.	4–11	complete*	614	2100
	IX	violet	4–9	nil	540	7300
	X	blue ppte.	4–11	insoluble	—	—
	XI	blue ppte.	4–11	insoluble	—	—

* Complex precipitates in isoamyl alcohol layer very soon after extraction from aqueous phase.

The spectral data for the copper(I) chelates do not show any obvious trend associated with ligand flexibility or rigidity. Copper(I) complexes of the ferroin and cuproine type are usually tetrahedral bis-chelates with bidentate ligands. Spatial requirements being less stringent in this case, differences in ligand flexibilities should not have as great an effect on the spectral properties of the copper(I) chelates as they do on the iron(II) chelates.

The structures of compounds III, IV, V, IX, X and XI suggest that these could give rise to polymeric chelates. Several (IX, X and XI) do form very insoluble coloured products with iron(II) and copper(I). The broad pH range of precipitation and insolubility in common solvents are properties typical of polymeric substances. It is curious, however, that the other three compounds do not behave similarly. More detailed studies are necessary to resolve the question.

According to steric arguments and various empirical studies,[5] compounds I, VI and VII should not be expected to give the characteristic intense colour reaction with iron(II) commonly referred to as the ferroin reaction. The experimental results confirm this expectation.

The quinoxaline derivatives of this study show little promise as colorimetric reagents for copper. The molar absorptivities of their copper(I) chelates are considerably less than those of other cuproine reagents currently in use. Stephen and Uden reached a similar conclusion regarding the chromogenic properties of some 26 derivatives of 2,3-bis(2-pyridyl)quinoxaline with respect to copper(I).[6]

Compounds III, IV and V show promise as colorimetric reagents for the determination of trace amounts of iron, but their synthesis is involved and expensive.

Acknowledgement—This investigation was supported by a grant from the G. Frederick Smith Chemical Company, and the compounds were provided by Dr. Francis H. Case.

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William C. Hoyle

Summary—Eleven pyrido and pyridyl derivatives of phenazine (6) and quinoxaline (5) have been examined as chromogens of the ferroin type for iron(II) and copper(I). Three of the quinoxaline derivatives show promise as reagents for iron(II) but are expensive and difficult to prepare.

Zusammenfassung—Elf Pyrido- und Pyridylderivate von Phenazin (6) und Chinoxalin (5) wurden als Farbreagentien vom Ferrointyp für Eisen(II) und Kupfer(I) untersucht. Drei von den Chinoxalinderivaten würden sich als Reagentien für Eisen(II) gut eignen, sind aber teuer und schwierig herzustellen.

Résumé—On a examiné onze dérivés pyrido et pyridyl de la phenazine (6) et de la quinoxaline (5) comme chromogènes du type ferroïne pour le fer(II) et le cuivre(I). Trois des dérivés de la quinoxaline sont prometteurs comme réactifs du fer(II) mais sont chers et difficiles à préparer.

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Phase titration with clarification end-point

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A rapid, routine experimental technique, not requiring elaborate instrumentation, was needed for the analysis of acetone–IBMK (isobutyl methyl ketone) mixtures. These compounds are not sufficiently different in density, refractive index, or other easily measurable physical properties to permit analysis by these means. It was therefore logical to consider phase titration with water or aqueous acetone. In the composition range of interest, however, the ternary binodal miscibility curve (Fig. 1) is approximately parallel to the IBMK–acetone side of the phase diagram, so that the classical method of phase titration is insensitive. In addition, the end-points are nearly invisible.

Although phase titration techniques for the analysis of binary systems have been known for a long time, little use is made of them, perhaps because many systems show the same insensitivity as the one described here. However, even when the sensitivity is adequate, the variations of end-point behaviour with sample composition restrict the precision of the method and limit the ranges of compositions over which it can be used.

Hitherto in phase titrations the appearance of cloudiness (indicative of a miscibility limit) has been taken as end-point. A third component miscible with only one of the binary components is added slowly to the clear binary solution (within an appropriate composition range) until the mixture

Compounds III, IV and V show promise as colorimetric reagents for the determination of trace amounts of iron, but their synthesis is involved and expensive.

Acknowledgement—This investigation was supported by a grant from the G. Frederick Smith Chemical Company, and the compounds were provided by Dr. Francis H. Case.

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Phase titration with clarification end-point

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A rapid, routine experimental technique, not requiring elaborate instrumentation, was needed for the analysis of acetone–IBMK (isobutyl methyl ketone) mixtures. These compounds are not sufficiently different in density, refractive index, or other easily measurable physical properties to permit analysis by these means. It was therefore logical to consider phase titration with water or aqueous acetone. In the composition range of interest, however, the ternary binodal miscibility curve (Fig. 1) is approximately parallel to the IBMK–acetone side of the phase diagram, so that the classical method of phase titration is insensitive. In addition, the end-points are nearly invisible.

Although phase titration techniques for the analysis of binary systems have been known for a long time, little use is made of them, perhaps because many systems show the same insensitivity as the one described here. However, even when the sensitivity is adequate, the variations of end-point behaviour with sample composition restrict the precision of the method and limit the ranges of compositions over which it can be used.

Hitherto in phase titrations the appearance of cloudiness (indicative of a miscibility limit) has been taken as end-point. A third component miscible with only one of the binary components is added slowly to the clear binary solution (within an appropriate composition range) until the mixture becomes turbid owing to the presence of a second phase. Bogin[1] analysed binary organic solutions by titration with water. Siggia and Hanna[2] used the method for the analysis of ternary systems, with one of the components determined independently. These and many other applications involve the crossing of binodal miscibility curves in the ternary systems at positions and angles which vary with the composition of the samples being analysed. The sharpness and intensity of the cloud-point is related to these factors. Caley and Habboush[3] described techniques for minimizing errors in titration of hydrocarbon–alcohol systems with water, and more recently, Rogers and co-authors[4–7] discussed the titration behaviour of ternary systems exhibiting a variety of solubility relationships. These authors find that, for a given system, the behaviour of the end-point varies so widely that only in a narrow segment of the composition range (typically 20–30%, see Fig. 2) can satisfactory end-points be obtained. In addition, the calibration curve is not geometrically simple in form and requires several calibration points for its determination.

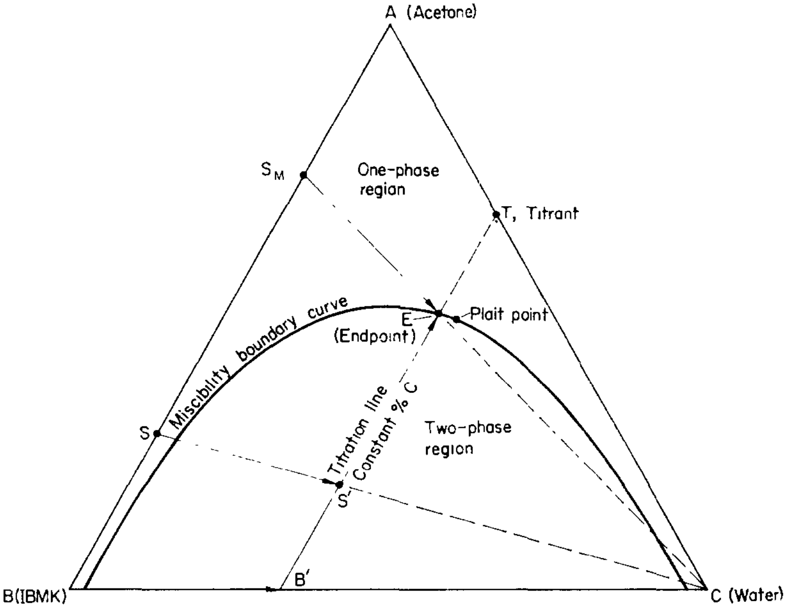

FIG. 1.—Ternary liquid-liquid miscibility diagram illustrating the analysis of the binary system *A–B* by phase titration.

None of the authors cited above used clarification end-points in lieu of the standard cloud end-point. Atwood,[8] however, has discussed the factors affecting the visibility of the end-point (as also have Rogers *et al.*) and has further discussed the use of both cloud and clarification end-points for the determination of ternary liquid–liquid equilibria. The most easily seen end-points (either cloud or clarification) are obtained by titration along a line through the binodal curve at or near the plait point and preferably as normal to the binodal curve as possible. The method described below permits titration through the binodal curve at the same point (near the plait point) and angle for all samples of the binary system being analysed. Hence, the precision can be maximized and is independent of sample composition.

Given a binary system of *A* and *B* (Fig. 1) and a third component, *C*, completely miscible with *A* but not *B*, it is possible to analyse for the fraction of *A* in any *A–B* mixture between pure *B* and composition S_M as follows: to an aliquot of the *A–B* sample (for example, of composition *S*) is added a given volume of *C*, such that all samples will have the same pre-defined concentration of *C* (for instance, 33% v/v), lying along the line *B'T*. The sample, now two-phase and therefore cloudy, is titrated (with stirring) with a mixture of *A* and *C* (composition *T*) having the same concentration of *C* as the adjusted sample (in this case 33% v/v). As the end-point *E* is approached, the mixture becomes more and more cloudy (due to increased dispersion), but at point *E* the cloud vanishes, giving a sharp end-point. The volume fraction, F_A, of *A* in the sample can be computed by

$$F_A = \frac{V_{tB} - V_{tS}}{V_{tB} + V_S} \qquad (1)$$

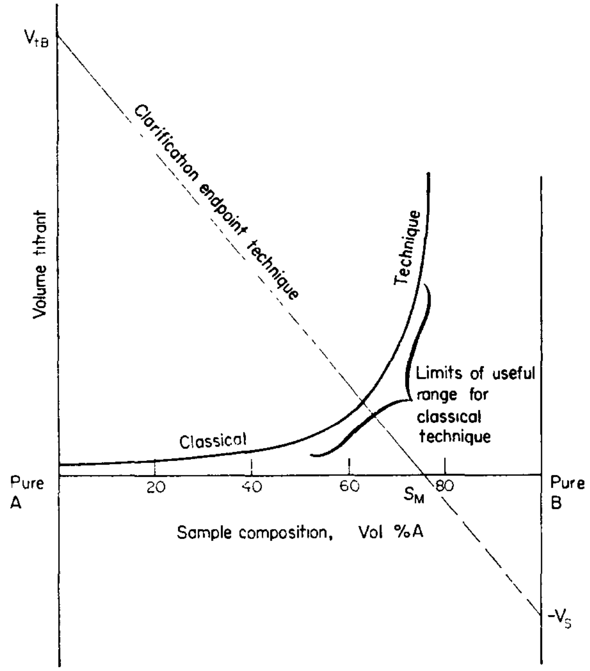

FIG. 2.—A comparison of the theoretical calibration curves for the classical and clarification end-point phase titration techniques.

where V_S is the sum of the volumes of sample aliquot and added C, V_{tB} is the volume of titrant needed for a sample of pure B, and V_{tS} is the volume of titrant required for the sample. Only one point, V_{tB}, is in theory required for the calibration of the method (see Fig. 2) although more might be required to identify and evaluate those secondary phenomena leading to deviations from equation (1) or from linearity (see below).

In its basic form, the method is limited to compositions between pure B and S_M. Coverage of the entire range, however, is possible by dilution of all samples with a fixed proportion (*e.g.*, an equal volume) of pure B. Such modified samples would be analysed as described, and the results obtained corrected back to give the original sample compositions. No similar procedure is possible to extend the range of the classical method, since the useful range does not generally extend to pure B, and the dilution required to bring some samples into the useful range would move others out of it.

Secondary effects

Small deviations from equation (1) can result from a number of causes, examples being changes in volume on mixing, thermal effects during titration, deviation of the titrant from its theoretically correct composition (such that titration is not precisely along a constant %-C line), or possibly traces of moisture or some other component in the samples or titrant. The first of these is significant in the acetone–IBMK–water system, inasmuch as the titrant density is higher than would be predicted for the ideal mixing of acetone and water. The actual volume of titrant, therefore, is equivalent to a larger volume of its components as measured on a before-mixing basis. There is no similar effect in the acetone–IBMK binary system, and as a result there is an apparent difference in the relative calibrations of the pipettes and the burette used for taking aliquots and for titration, respectively. The over-all effect, while not strictly linear, is sufficiently so within the precision of the titration to permit a linear correction to equation (1), of the form

$$\Delta V_{tS} = KF_A \tag{2}$$

which leads to

$$F_A = \frac{V_{tB} - V_{tS}}{V_t^B + V_S + K}. \tag{3}$$

Hence, the constant K behaves as though it were a correction to V_S, *i.e.*, it adjusts the volume of the sample to be consistent with the "erroneous" burrette (though the error is not really in the burette, but in the titrant density). It is expected that those types of secondary phenomena encountered with other systems can be handled as easily, since the primary effect of such phenomena is only a change in the slope of the calibration line, deviations from linearity being secondary and of significance only in extreme cases.

EXPERIMENTAL

Three standard solutions of 100·00, 75·00, and 50·00% v/v IBMK in acetone were prepared for calibration purposes, and a titrant of 33·3% v/v water in acetone was made up. Reagent grade IBMK and acetone and distilled water were used throughout.

To a 125-ml Erlenmeyer flask, 10·0 ml of sample and 5·0 ml of water were transferred with volumetric pipettes. A magnetic stirring bar was added and the flask was covered with a two-hole rubber stopper, through which passed the tip of a 50·0-ml burette. An insulating sheet was placed between the magnetic stirrer and the titration flask to prevent heating from the motor. The sample was titrated to the disappearance of turbidity. The end-point was quite sharp and could be easily discriminated within 1–2 drops of titrant.

TABLE I.—CALIBRATION OF THE PHASE TITRATION OF ACETONE–IBMK SOLUTIONS

Sample composition % v/v IBMK	Titration volume, *ml*	
100·00	44·42	
	44·27	Mean = 44·28
	44·17	s = 0·103
	44·27	
75·00	29·67	
	29·62	Mean = 29·63
	29·60	s = 0·036
50·00	15·05	
	15·00	Mean = 15·05
	15·10	s = 0·050

s = standard deviation.

The three standards, together with several unknowns, were sampled and titrated in random order and in replicate, all titrations being performed during the course of a single day. The results for the standards are given in Table I. The standard deviation for all samples (including the unknowns) was 0·07 ml, corresponding to 0·12% acetone.

From the results for the three standards, the values of V_{tB} and K were computed to be 44·28 ml and −0·82 ml respectively. Apparent deviation from linearity was at most only 0·03 ml, much less than the standard deviation, and hence statistically insignificant.

Solutions of water in acetone were titrated by a similar method. To 5 volumes of sample 1 volume of IBMK was added, shifting the compositions to the 16·6% v/v IBMK line. The mixture was then titrated with a solution of 16·6 % v/v IBMK in acetone. An equally sharp end-point was obtained.

DISCUSSION

The procedure described greatly widens the scope of phase titrations for the analysis of binary systems. The application of the method to systems other than acetone–IBMK is quite straightforward. If a phase diagram is available for an appropriate ternary system (which includes the binary system in question), the position of the plait point on this diagram will define the approximate titrant composition and the volume of the third component to be added to the sample aliquots. However, a phase diagram is not really necessary. If a third component can be found which is known (or suspected) to be of the proper type, *i.e.*, will lead to a single closed binodal curve in the ternary system, titration along any of several constant %-C lines can be tried. The method is perfectly feasible (and essentially with linear response) whether the titration line passes close to the plait point or not. However, titration lines passing closest to the plait point will give the sharpest end-points.

In the development of a method without the aid of a phase diagram, a sample of pure B, to which a selected quantity of C had been added, would be titrated with the comparable A–C titrant. From V_{tB} and V_S, a straight line could then be drawn, as in Fig. 2, intersecting the abcissa at S_M, thus delineating the range over which the selected titration line would be useful without modification, or defining the ratio in which all samples would be diluted with *B* in order to cover the entire binary range. If the selected titration line proved satisfactory, one or more additional points would then be obtained with standards (appropriately further diluted with *B* if the full range modification is chosen) to establish the precise slope of the calibration line, with secondary phenomena taken into account.

The method should also be applicable to the analysis of pseudo-binary systems. For example, the ratio of aromatics to non-aromatics in hydrocarbon mixtures could be estimated by addition of aniline followed by titration with an aniline–aromatics solution. Such a procedure would be much simpler than the usual "aniline point" method which requires that the sample be heated and/or cooled.

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Summary—An improved method of phase titration has been developed for the analysis of binary or pseudo-binary systems. A clarification end-point is used in place of the usual cloud end-point. Advantages are that end-points are equally sharp over a wide sample composition range, the titration volume is a very nearly linear function of composition so that often only one calibration point is needed, and the technique can be extended to cover the entire binary composition range.

Zusammenfassung—Eine verbesserte Methode der Phasentitration zur Analyse binärer oder pseudobinärer Systeme wurde entwickelt. Statt des üblichen Trübungs-Endpunktes wird ein Klärungs-Endpunkt verwendet. Die Vorteile bestehen in folgendem: die Endpunkte sind in einem weiten Bereich der Probenzusammensetzung gleich scharf; das Titrationsvolumen ist in sehr guter Näherung eine lineare Funktion der Zusammensetzung, sodaß oft nur ein Eichpunkt notwendig ist; das Verfahren kann über den ganzen binären Mischungsbereich ausgedehnt werden.

Résumé—On a élaboré une méthode améliorée de titrage de phase pour l'analyse de systèmes binaires ou pseudo-binaires. On utilise un point final de clarification au lieu du point final de trouble usuel. Les avantages en sont que les points de fin de dosage sont également nets dans un large domaine de composition de l'énchantillon, le volume de titrage est une fonction très sensiblement linéaire de la composition de sorte qu'un seul point d'étalonnage est souvent nécessaire, et l'on peut étendre la technique pour couvrir tout le domaine de composition binaire.

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Thin-layer chromatographic separation of scandium, yttrium, the rare earths, thorium and uranium(VI)

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THE paper chromatographic separation of uranium, thorium and the rare earths from each other, which is of considerable interest in the field of nuclear chemistry, has already been accomplished by many investigators using both normal and reversed-phase techniques. However, there is less information about the separation of these metal ions from each other by thin-layer chromatography in spite of the advantages of rapidity and higher capacity. Thin-layer chromatographic separations involving scandium, the rare earths, thorium and uranium have scarcely ever been carried out by normal[1] but mostly by reversed-phase chromatography.[2-4]

The present work was undertaken to find more simple and effective normal thin-layer chromatographic systems for the separation of scandium, yttrium, the rare earths, thorium and uranium(VI). By eluting with a mixture of dioxan and hydrochloric acid or nitric acid on cellulose thin-layer plates, we have achieved many useful separations including scandium–yttrium–lanthanum; uranium(VI)–thorium–rare earths; scandium–thorium–rare earths; thorium–yttrium–lanthanum; and uranium(VI)–scandium–yttrium. Separations of the rare earths among themselves, however, were obtained only for some selected non-adjacent pairs.

EXPERIMENTAL

The test solutions were prepared by dissolving scandium, yttrium and rare earth oxides, and thorium and uranium(VI) nitrates, respectively, in 1*M* hydrochloric acid. The metal ion concentration of each solution was 0·1*M*.

MN cellulose powder 300 (Macherey, Nagel & Co., Düren, Germany) (15 g) was thoroughly blended with demineralized water (90 ml) in a fast electric mixer for 4 min. The mixture was immediately spread 250 μ thick on 10 × 20 cm glass plates. The plates were dried first in air for 1 hr and then in an oven at 100–105° for 30 min. The plates so prepared were placed in a desiccator over silica gel until ready for use.

About 0·2 μl of a test solution was spotted with a glass capillary, at 2·5 cm from one end of the plate, and dried in air for 30 min. Development was carried out at 26–28° by the ascending technique until the solvent front had risen 10 cm. The developing solvents tested were:

(*a*) dioxan-12*M* HCl (7:3) (*d*) dioxan-14*M* HNO_3 (7:3)

(*b*) dioxan-12*M* HCl (1:1) (*e*) dioxan-14*M* HNO_3 (1:1)

(*c*) dioxan-12*M* HCl (3:7) (*f*) dioxan-14*M* HNO_3 (3:7)

Subsequently, the plates were dried in air and the spots of metal ions located by spraying with a 0·1% aqueous solution of Arsenazo III. Yttrium, the rare earths, thorium and uranium(VI) formed green spots on the pink background. The violet spot of scandium appeared gradually about 30 min after spraying of the reagent. The spots of all metal ions remained stable for several days.

RESULTS AND DISCUSSION

The results of the experiments on the behaviour of scandium, yttrium, the rare earths, thorium and uranium(VI) under various conditions of thin-layer chromatography are summarized in Table I. The R_f values of the front and rear limits of the spots are given.

For the dioxan–hydrochloric acid system, R_f values of uranium(VI) and scandium decrease with increasing ratio of hydrochloric acid to dioxan, while those for the rare earths including yttrium increase. R_f values for thorium are only affected slightly by variation in the dioxan–hydrochloric acid ratio. Therefore, with this solvent system, the rare earths, thorium and uranium(VI) give markedly different R_f values, which permits good separations, particularly when a lower ratio of hydrochloric acid to dioxan is used. Procedures for individual separations are given in Table II. Differences between R_f values are satisfactory, but the spots of thorium are somewhat diffuse. The spread of thorium spots can easily be reduced by increasing the hydrochloric acid–dioxan ratio. In most cases pairs or groups of metal ions in widely different proportions may be completely separated. Thorium and uranium(VI), thorium and lanthanum, and uranium(VI) and lanthanum can be separated effectively in proportions ranging from 1:100 to 100:1.

TABLE I.—R_f VALUES FOR SCANDIUM, YTTRIUM, THE RARE EARTHS, THORIUM AND URANIUM(VI) IN VARIOUS SOLVENT SYSTEMS

Solvent systems	Developing time, hr	R_f values						
		Sc	Y	La	Sm	Lu	Th	U(VI)
1. Dioxan-12*M* HCl (7:3)	2·8	0·77–0·84	0·24–0·35	0·06–0·19	0·15–0·29	0·26–0·36	0·44–0·72	0·87–0·97
2. Dioxan-12*M* HCl (1:1)	3·8	0·71–0·78	0·45–0·53	0·26–0·36	0·34–0·43	0·42–0·49	0·49–0·62	0·80–0·88
3. Dioxan-12*M* HCl (3:7)	4·0	0·70–0·77	0·59–0·67	0·42–0·49	0·49–0·56	0·58–0·65	0·57–0·67	0·71–0·80
4. Dioxan-14*M* HNO_3 (7:3)	1·5	0·76–0·91	0·49–0·61	0·40–0·53	0·48–0·59	0·59–0·70	0·86–1·00	0·88–1·00
5. Dioxan-14*M* HNO_3 (1:1)	2·2	0·69–0·75	0·52–0·58	0·48–0·56	0·50–0·59	0·54–0·61	0·87–0·98	0·88–0·98
6. Dioxan-14*M* HNO_3 (3:7)	2·3	0·68–0·76	0·62–0·68	0·63–0·70	0·62–0·68	0·61–0·68	0·83–0·92	0·83–0·93

TABLE II.—SEPARATIONS

Solvent systems	Mixtures, μg	R_f values
Dioxan-12M HCl (7:3)	Sc(0·3)–Y(0·6)–La(0·9)	Sc(0·77–0·86):Y(0·23–0·36):La(0·06–0·17)
	Sc(0·3)–Th(1·5)–Sm(1·0)	Sc(0·78–0·86):Th(0·51–0·75):Sm(0·15–0·27)
	Sc(0·3)–Lu(1·2)–La(0·9)	Sc(0·78–0·86):Lu(0·21–0·35):La(0·06–0·17)
	U(VI)(1·6)–Th(1·5)–Lu(1·2)	U(VI)(0·84–0·96):Th(0·49–0·75):Lu(0·22–0·34)
	Th(1·5)–Y(0·6)–La(0·9)	Th(0·51–0·75):Y(0·23–0·36):La(0·06–0·17)
	Th(0·1)–La(10)	Th(0·54–0·67):La(0·05–0·21)
	Th(10)–La(0·1)	Th(0·41–0·73):La(0·09–0·16)
	U(VI)(0·1)–La(10)	U(VI)(0·87–0·95):La(0·05–0·21)
	U(VI)(10)–La(0·1)	U(VI)(0·85–0·98):La(0·09–0·16)
Dioxan-14M HNO_3 (7:3)	Th(1·5)–Sc(0·3)–Sm(1·0)	Th(0·93–1·00):Sc(0·75–0·86):Sm(0·55–0·63)
	Th(1·5)–Sc(0·3)–La(0·9)	Th(0·94–1·00):Sc(0·76–0·86):La(0·55–0·64)
	Th(2·3)–Lu(1·8)	Th(0·94–1·00):Lu(0·60–0·70)
	U(VI)(1·6)–Sc(0·3)–Y(0·6)	U(VI)(0·94–1·00):Sc(0·75–0·86):Y(0·56–0·65)
Dioxan-14M HNO_3 (1:1)	Th(0·1)–Sc(10)	Th(0·85–0·96):Sc(0·65–0·77)
	U(VI)(0·1)–Sc(10)	U(VI)(0·85–0·99):Sc(0·65–0·77)
Dioxan-12M HCl (1:1)	U(VI)(10)–Th(0·1)	U(VI)(0·80–0·90):Th(0·51–0·60)
	U(VI)(0·1)–Th(10)	U(VI)(0·82–0·89):Th(0·45–0·63)

It is worth noting that a selected pair of rare earths, such as lanthanum and lutetium, is also separated very easily with this solvent system. A survey of the behaviour of individual rare earths in dioxan–hydrochloric acid (7:3 and 1:1) systems indicates that R_f values for the rare earths increase slowly with increasing atomic number, reaching a nearly constant value at dysprosium. This form of R_f "spectrum" does not change with the variation in relative amounts of dioxan and hydrochloric acid.

R_f values for scandium, yttrium, the rare earths, thorium and uranium(VI) in dioxan-14*M* nitric acid systems are also tabulated in Table I. The nitric acid–dioxan ratio is not as critical as that of dioxan to hydrochloric acid. Even though the separation of uranium(VI) and thorium is difficult, there are still sufficient differences in R_f values of uranium(VI), thorium, scandium, and the rare earths in this solvent system for many separations to be achieved.

The results of such separations are shown in Table II. Useful separations involving widely different proportions of scandium to uranium(VI) and scandium to thorium are easily accomplished. Measurements of R_f values for the individual rare earths in dioxan–14*M* nitric acid (7:3) suggest that a selected pair of the rare earths, *i.e.*, lanthanum and a rare earth heavier than erbium, should be separated even in this solvent system.

It is of interest to note that the eluting solutions presented here allow the rare earths and thorium, and scandium and thorium to be separated very easily: these separations are actually impossible even with anion-exchange in hydrochloric acid solutions of varying concentrations. Besides this, the eluting solutions reported here may also find further use in normal phase paper chromatography, in which traditional mixtures of mineral acids and alcohols have been employed almost exclusively.

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Summary—The chromatographic behaviour of scandium, yttrium, the rare earths, thorium and uranium(VI) in dioxan–hydrochloric acid and dioxan–nitric acid media on a plain cellulose thin layer has been investigated. The following separations are possible: scandium–yttrium–lanthanum, scandium–samarium–thorium, scandium–lanthanum–lutetium, yttrium–lanthanum–thorium, and lutetium–thorium–uranium(VI) with dioxan–12*M* hydrochloric acid (7:3) and scandium–samarium–thorium, scandium–yttrium–uranium(VI), lutetium–thorium, and scandium–lanthanum–thorium with dioxan–14*M* nitric acid (7:3). A single chromogenic spray (Arsenazo III) has been used for the detection of all the metal ions studied.

Zusammenfassung—Das chromatographische Verhalten von Scandium, Yttrium, den seltenen Erden, Thorium und Uran(VI) in Medien aus Dioxan und Salzsäure sowie Dioxan und Salpetersäure wurde auf einer Cellulose-Dünnschicht untersucht. Folgende Trennungen sind möglich: Scandium–Yttrium–Lanthan, Scandium–Samarium–Thorium, Scandium–Lanthan–Lutetium, Yttrium–Lanthan–Thorium sowie Lutetium–Thorium–Uran(VI) mit Dioxan: 12*M* Salzsäure (7:3) und Scandium–Samarium–Thorium, Scandium–Yttrium–Uran(VI), Lutetium–Thorium und Scandium–Lanthan–Thorium mit Dioxan: 14*M* Salpetersäure (7:3). Ein einziger Entwicklerspray (Arsenazo III) wurde zum Nachweis aller untersuchter Metallionen verwendet.

Résumé—On a étudié le comportement chromatographique de: scandium, yttrium, les terres rares, thorium et uranium(VI) en milieux dioxane–acide chlorhydrique et dioxane–acide nitrique sur une couche mince de cellulose ordinaire. Les séparations suivantes sont possibles: scandium–yttrium–lanthane, scandium–samarium–thorium, scandium–lanthane–lutétium, yttrium–lanthane–thorium et lutétium–thorium–uranium(VI) par le dioxane–acide chlorhydrique 12*M* (7:3) et scandium–samarium–thorium, scandium–yttrium–uranium(VI), lutétium–thorium et scandium–lanthane–thorium par le dioxane–acide nitrique 14*M* (7:3). On a utilisé une seule pulvérisation de chromogène (Arsenazo III) pour la détection de tous les ions métalliques étudiés.

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Spectrophotometric determination of tetrafluoroborate with ferroin

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RELATIVELY few methods for the direct determination of the tetrafluoroborate anion have been reported in the literature. Lange[1] precipitated this anion as the nitron salt but did not develop a systematic gravimetric method. Later, Lucchesi and DeFord[2] developed a procedure for precipitation as the nitron salt. Schaack and Wagner[3] developed an indirect titrimetric method with cetyltrimethylammonium chloride as precipitant. Coursier, Hure, and Platzer[4] developed a method involving extraction of tetraphenylarsonium tetrafluoroborate into chloroform; the tetrafluoroborate was then converted back into borate which was determined spectrophotometrically with curcumin. Archer and Affsprung[5] developed both a gravimetric and an indirect spectrophotometric method using tetraphenylarsonium chloride as a reagent.

Ferroin, tris(1,10-phenanthroline)iron(II) sulphate, has been used previously as a spectrophotometric reagent for the determination of perchlorate,[6,7] iodide,[8] hexafluorophosphate,[9] hexafluoroarsenate,[10] and hexafluoroantimonate[11] by selective extraction of the ferroin salt of the anion into either nitrobenzene or n-butyronitrile and subsequent measurement of the absorbance of the organic extract in the range 500–520 mμ.

The same method is now applied to tetrafluoroborate.

EXPERIMENTAL

Reagents

A 0·01*M* solution of ferroin was prepared from iron(II) sulphate and 1,10-phenanthroline. A series of standard solutions of ammonium tetrafluoroborate was prepared from NH_4BF_4 previously analysed by the gravimetric method of Affsprung and Archer.[5] Owing to the fact that ammonium tetrafluoroborate undergoes slow hydrolysis, these solutions were used within an hour of preparation. n-Butyronitrile was obtained from Eastman Organic Chemicals and used without purification.

Calibration curve

Mix 2·500 ml of solution containing 0·4–14 μmole of tetrafluoroborate with 2 ml of 0·01*M* ferroin in a 15-ml glass-stoppered centrifuge tube. Add 5 ml of n-butyronitrile and shake the mixture vigorously for 2 min. Centrifuge for 2 min to separate the phases. Take a 1-ml aliquot of the organic (upper) layer, and dilute it to volume with n-butyronitrile in a 5-ml volumetric flask. Measure the absorbance of this solution immediately in a 1-cm cell against pure n-butyronitrile at 520 mμ; using a 0·1-mm slit-width (on a Beckman DU spectrophotometer). Plot the calibration curve.

Development of method

Two ml of 0·01*M* ferroin were added to a 2·50-ml aliquot of solution containing 0·3–8 μmole of tetrafluoroborate and the mixture was extracted with four 5-ml portions of n-butyronitrile. The extracts were combined and diluted to volume with n-butyronitrile in a 25-ml volumetric flask, and the absorbance of this solution was measured at 520 mμ in a 1-cm cell. The dilution factors made the absorbances obtained in single and multiple extraction procedures directly comparable.

The colour stability was investigated in the usual way. The effect of pH on the extraction was determined over the range pH 2–10, with two different fluoroborate concentrations.

A series of anions was tested for interference, by adding 0·20 mmole of an alkali metal salt of the anion to the aqueous fluoroborate solution and extracting. Sodium chloride, sodium acetate and potassium fluoride were tested for interference at a series of higher concentrations.

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Spectrophotometric determination of tetrafluoroborate with ferroin

(*Received* 11 *December* 1967. *Revised* 6 *February* 1968. *Accepted* 1 *March* 1968)

RELATIVELY few methods for the direct determination of the tetrafluoroborate anion have been reported in the literature. Lange[1] precipitated this anion as the nitron salt but did not develop a systematic gravimetric method. Later, Lucchesi and DeFord[2] developed a procedure for precipitation as the nitron salt. Schaack and Wagner[3] developed an indirect titrimetric method with cetyltrimethylammonium chloride as precipitant. Coursier, Hure, and Platzer[4] developed a method involving extraction of tetraphenylarsonium tetrafluoroborate into chloroform; the tetrafluoroborate was then converted back into borate which was determined spectrophotometrically with curcumin. Archer and Affsprung[5] developed both a gravimetric and an indirect spectrophotometric method using tetraphenylarsonium chloride as a reagent.

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The same method is now applied to tetrafluoroborate.

EXPERIMENTAL

Reagents

A 0·01M solution of ferroin was prepared from iron(II) sulphate and 1,10-phenanthroline. A series of standard solutions of ammonium tetrafluoroborate was prepared from NH_4BF_4 previously analysed by the gravimetric method of Affsprung and Archer.[5] Owing to the fact that ammonium tetrafluoroborate undergoes slow hydrolysis, these solutions were used within an hour of preparation. n-Butyronitrile was obtained from Eastman Organic Chemicals and used without purification.

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A series of anions was tested for interference, by adding 0·20 mmole of an alkali metal salt of the anion to the aqueous fluoroborate solution and extracting. Sodium chloride, sodium acetate and potassium fluoride were tested for interference at a series of higher concentrations.

RESULTS AND DISCUSSION

Seventeen ammonium tetrafluoroborate samples in the range 0·443–13·74 μmole were analysed by the single extraction procedure. Beer's law was obeyed over this concentration range. A least-squares analysis showed the slope of the calibration line to be 0·164 μmole^{-1}. cm^{-1} with a standard deviation of 0·0013 μmole^{-1}. cm^{-1}. The exhaustive extraction procedure was used on nine ammonium tetrafluoroborate samples in the range 0·334–7·67 μmole. The slope of the exhaustive calibration line was found to be 0·221 μmole^{-1}. cm^{-1} with a standard deviation of 0·0026 μmole^{-1}. cm^{-1}. Therefore 74·3 % of the tetrafluoroborate was extracted in a single extraction. It was found that the colour of the extracts faded at a moderately fast rate (see Tables I and II) as also occurred in the previously developed methods for hexafluorophosphate,[9] hexafluoroarsenate,[10] and hexafluoroantimonate.[11] It would therefore seem imperative that the extractions and measurements be made quickly. It was found that pH variations between 2·2 and 10·6 had no appreciable effect on the extraction. However, it should be mentioned that the extractions were made very shortly after the solution was buffered at the desired pH. If the solutions should be allowed to stand at a low pH for very long, interference might occur, owing to acid catalysis of the hydrolysis reaction of the tetrafluoroborate anion. Anion interferences are shown in Table II. It should be mentioned that fluoride and borate ions, which do not interfere singly, might interfere jointly in strongly acid medium owing to their reacting to produce more fluoroborate anion. This danger can be eliminated by keeping the solution in the pH region 6–8. Sodium chloride, sodium acetate and potassium fluoride exhibit slight negative interferences at higher concentrations.

TABLE I.—STABILITY STUDY ON EXTRACTS

NH_4BF_4, *μmole*	Absorbance after			
	0 hr	½ hr	4 hr	8 hr
0·85	0·166	0·154	0·140	—
1·72	0·318	0·305	0·279	—
2·56	0·459	0·444	0·434	0·426
3·41	0·598	0·586	0·562	0·560
4·27	0·747	0·733	0·733	0·728

TABLE II.—ANION INTERFERENCE

Compound used	Degree of interference*	Compound used	Degree of interference*
$KHC_8H_4O_4$	Strong, positive	NH_4Cl	Moderate, negative
Na_2HBO_3	None	KIO_3	None
$NaBO_2$	None	KNO_2	Strong, positive
Na_2PO_3F	None	$K_2Cr_2O_7$	Slight, negative
Na_2CO_3	None	Na_2SO_4	Slight, negative
Na_2SO_4	Slight, negative	Na_2SO_3	Slight, negative
$Na_2C_2O_4$	Slight, negative	NaCl	None
Na_2HPO_4	None	KBr	Strong, positive
NaH_2PO_4	Slight, negative	KNO_3	Strong, positive
Na_3PO_4	Slight, negative	KSCN	Strong, positive
$NaKC_4H_4O_6 \cdot 4H_2O$	Slight, negative	$NaC_2H_3O_2$	None
KF	None		

* Key to notation:
0–2 %—None
2–5 %—Slight
5–10 %—Moderate
>10 %—Strong

This method will give the most reliable results if the solutions are kept near neutrality and are analysed very soon after being prepared. The method is by far the fastest for tetrafluoroborate determination, but is limited by the precision (1% at best) of the classical methods for analysis of the ammonium tetrafluoroborate used for calibration. It is to be hoped that more precise methods will be developed in the near future.

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Summary—A spectrophotometric method for determination of the tetrafluoroborate anion with ferroin is described. The ferroin tetrafluoroborate is selectively extracted in the presence of excess of ferroin into n-butyronitrile, and the absorbance of the organic extract is measured at 520 mμ. Beer's law is followed over a wide range of tetrafluoroborate concentrations when a single extraction procedure is used. Exhaustive extractions indicate that 74% of the tetrafluoroborate is removed in a single extraction.

Résumé—On décrit une méthode spectrophotométrique pour le dosage de l'anion tétrafluoroborate au moyen de ferroïne. Le tétrafluoroborate de ferroïne est extrait sélectivement en la présence de l'excès de ferroïne en *n*-butyronitrile et l'on mesure l'absorption de l'extrait organique à 520 mμ. Lorsqu'on utilise une seule technique d'extraction, la loi de Beer est suivie dans un large domaine de concentrations en tétrafluoroborate. Des extractions exhaustives montrent que 74% du tétrafluoroborate sont éliminés en seule extraction.

Zusammenfassung—Eine spektrophotometrische Methode zur Bestimmung des Tetrafluoroborat-Anions mit Ferroin wird beschrieben. Das Ferroin-Tetrafluoroborat wird in Gegenwart eines Überschusses von Ferroin selektiv in n-Butyronitril extrahiert und die Extinktion des organischen Extraktes bei 520 nm gemessen. Das Beersche Gesetz wird in einem weiten Bereich von Tetrafluoroborat-Konzentrationen befolgt, wenn man nur eine Extraktion vornimmt. Erschöpfende Extraktionen zeigen, daß bei einer Extraktion 74% des Tetrafluoroborats entfernt werden.

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Determination of scandium in sea-water by atomic-absorption spectroscopy

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THE study of trace elements in marine chemistry and geochemistry requires rapid, simple and sensitive methods of determination, producing accurate results. Atomic-absorption spectroscopy is one such method, and has been used by Fabricand *et al.*[1] to determine directly copper, iron, manganese, nickel and zinc in sea-water samples without preconcentration. Magee and Rahman[2] determined copper in sea-water by atomic-absorption spectroscopy, using ammonium pyrrolidinedithiocarbamate to complex the copper. Recently Joyner and Finley[3] employed a diethyldithiocarbamate–isobutyl methyl ketone extraction system to determine manganese and copper in sea-water. In all these determinations, the sensitivity reached the parts per thousand million level.[9]

Scandium in sea-water was first determined by Wattenburg[4] who found 0·04 μg/l. by a spectrographic method. Later Shigematsu *et al.*[5] found 0·004 μg/l. in Japanese coastal waters, using calcium oxalate as carrier for collecting scandium, followed by a spectrophotometric method. The process was developed by isotope techniques to assure quantitative recovery. These two values show a discrepancy of a factor of ten.

Since the occurrence of scandium is extremely rare in the earth's crust, its scarcity in sea-water is to be expected, and a concentration step is therefore necessary before its determination. As large samples are used, extraction techniques seemed to be inconvenient and co-precipitation or co-crystallization appeared more appropriate.

Concentration of scandium from sea-water

Several methods of collecting scandium from sea-water were investigated by radiometric techniques, ^{46}Sc(III) being used as tracer. When a litre of filtered sea-water spiked with ^{46}Sc and adjusted to pH 5 with an acetate buffer was passed through a column (15 × 100 mm) packed with a chelating resin (Chelex-100, 50–100 mesh) and eluted with 0·1*M* EDTA, 75–80% of the scandium activity was recovered. No further improvement in recovery was obtained by altering the pH of the sample or the concentration of the eluting agent. A longer column lowered the elution rate without increasing the uptake efficiency. The ion-exchange method of concentration was not further investigated.

The co-precipitation of scandium with various hydrous oxides was then investigated. The sea-water sample (3 l.) was first acidified to pH 2 with hydrochloric acid, filtered through a membrane of 0·5 μ porosity, and equilibrated with *ca.* 0·2 μC of ^{46}Sc(III) containing *ca.* 0·5 μg of scandium as carrier. Hydrous oxides of iron(III), indium(III) and aluminium(III) were precipitated by the addition of a salt of the corresponding ion (30 mg) followed by adjustment of the sea-water to various pH values. Hydrous manganese dioxide was produced by adding potassium permanganate and ethanol to the sea-water sample. The hydroxide precipitates were separated after settling by decantation and centrifugation, and dissolved in hydrochloric acid. Manganese dioxide was dissolved in sulphurous acid. The recovery of scandium was determined by counting the γ-activity of the solution and comparing it with a control standard of the same volume. Of the hydrous oxides studied, that of iron(III) was found to recover quantitatively microgram quantities of scandium at a pH above 8 (Table 1). Maximum recoveries of 80%, 85% and 75% at pH 8·5, 9·0 and 8·0 respectively were found with the oxides of manganese, indium and aluminium.

TABLE I.—RECOVERY OF ^{46}Sc(III) FROM SEA-WATER BY HYDROUS IRON(III) OXIDE

pH	9·5	9·1	8·4	7·8	7·3	6·6	5·0	4·0
% Recovery	101	99	100	99	93	88	69	15

Separation of scandium from the precipitant

Atomic-absorption spectroscopy does not suffer from chemical interference, but presence of large amounts of anions and cations can cause pronounced effects on the absorption (Elwell and Gidley[6]). As concentrations of iron above 2000 ppm lowered the absorption signal of scandium significantly, the removal of the iron was desirable.

The readiness of iron(III) to form chloro-complexes in concentrated hydrochloric acid, whereas scandium remains as a cationic species, provides a possibility of separation by ion-exchange. The separation was studied with 2 μg of scandium labelled with ^{46}Sc and 30 mg of iron in concentrated hydrochloric acid loaded into a column of anion-exchange resin in the chloride form. The column was successively eluted with 10-ml portions of concentrated hydrochloric acid, and the effluent fractions were radiometrically assayed. It was found that the first 60 ml of the eluate contained all the scandium activity while the iron was completely retained by the resin.

The total effluent was evaporated to dryness on a steam-bath. A pale yellow organic residue was left which was probably the organic matter concentrated from sea-water or the debris from the resin. It did not show any absorption interference with the spectral line of scandium. The evaporation involved no loss of scandium, as indicated by the ^{46}Sc tracer activity.

Atomic-absorption spectroscopy of scandium

The optimum conditions and the extraction procedure for the determination of trace amounts of scandium as recommended by Chau[7] were used in the present work. The sensitivity was enhanced by extracting the scandium into an oxine–butanol solution. A detection limit of 0·06 ppm of scandium was reported, a nitrous oxide–acetylene flame being used.

No interference was experienced in the absorption measurement of 4 ppm of scandium in the presence of 200 ppm of each of the following ions: Fe(III), Ni, Co(II), Cu(II), Mo(VI), Cr(III), Na, Mg and Ca. All these concentrations exceed by far the possible contamination in the co-precipitation process.

EXPERIMENTAL

Reagents

Iron(III) *chloride solution*. Dilute an analytical reagent grade stock solution to give a solution containing 2 mg of iron/ml.

Hydrochloric acid. Distil analytical grade hydrochloric acid and further saturate the distillate with hydrogen chloride generated by distilling concentrated hydrochloric acid.

Scandium standard solution. Dissolve high purity grade scandium oxide in a small amount of warmed hydrochloric acid. Evaporate on a water-bath to remove excess of acid. Dissolve the residue in 0·1*M* hydrochloric acid to give a stock solution of 100 μg of Sc/ml. Prepare a working standard of 2 μg/ml by dilution.

Ion-exchange resin. Anion-exchange resin Permutit De-Acidite FF-IP (SRA 71) 100–200 mesh in chloride form was washed several times with 6*M* hydrochloric acid and packed into a column 120 × 15 mm. The resin was conditioned by being washed several times with 20-ml portions of concentrated hydrochloric acid. The resin deteriorated after repeated use and was replaced after two runs.

Wash-liquid. Dissolve 5 g of ammonium nitrate in 1 l. of distilled water and adjust the pH of solution to pH 8–9 with ammonia.

^{46}Sc(III). Supplied by the Radiochemical Centre, Amersham, England.

Apparatus

A Techtron A.A.4 atomic-absorption spectrophotometer used with a high-temperature burner, model AB-40, with a 5-cm flame path. A scandium hollow-cathode lamp was supplied by Atomic Spectral Lamps Pty. Ltd. Australia.

Instrument conditions for atomic-absorption spectroscopy of scandium: spectral line 3913·5 Å; cathode lamp current 10 mA; flame mixture acetylene flow-meter reading 9·5, nitrous oxide 20 psi; monochromator slit 50 μ; 5 × scale expansion.

Determination of scandium in sea-water

Acidify the sample (20 l.) to pH 2 immediately after collection, by addition of dilute hydrochloric acid. Filter through a membrane filter (0·5 μ), and add a solution containing 80 mg of iron. Adjust the pH to 8–9 with 2*M* ammonia, shake well and allow the precipitate to settle over-night. Syphon the clear supernatant liquid through a glass fibre filter and centrifuge the rest in 50-ml centrifuge tubes. Wash the precipitate on the filter with 10-ml portions of 0·5 % ammonium nitrate solution and that in the centrifuge tubes with three 20-ml portions of wash-liquid, centrifuging and decanting after each wash. Dry the precipitates in the centrifuge tubes on a steam-bath. Dissolve the precipitates on the glass filter and in the centrifuge tubes in 20 ml of concentrated hydrochloric acid, and pass the solution through the ion-exchange column. Elute the scandium from the column with 150 ml of concentrated hydrochloric acid and evaporate the eluate to dryness. Dissolve the residue in *ca*. 3 ml of 0·01*M* hydrochloric acid and adjust the pH to 2–4 with dilute acetic acid and sodium acetate. Transfer the solution to a 15-ml separating funnel and extract with 3 ml of 2·5 % oxine in butanol for 1 min. Separate the layers by centrifugation and draw the alcohol layer into a

3-ml volumetric flask. Make up to the mark to compensate for the butanol lost by dissolution in the water. Spray the solution into the flame for absorption measurement.

The blank from running the whole process on scandium-free sea-water was extremely low when measured against pure butanol. Since the iron(III) chloride reagent contains no detectable scandium, the blank may be prepared by running a similar amount of hydrochloric acid through the ion-exchange column, evaporating to dryness, and extracting with oxine in butanol. A standard is run by extracting 6 μg of scandium at pH 2–4 with 3 ml of oxine–butanol solvent, and making up to 3 ml after extraction. The atomic-absorption reference blank is pure butanol, and all absorption measurements are made with respect to it. The absorption response is linear up to 5 μg of sc/ml.

RESULTS AND DISCUSSION

Recovery of scandium from sea-water

The recovery of scandium from sea-water was checked by radiometric and chemical methods. In the radiometric method, ^{46}Sc with *ca.* 1 μg of carrier was added to 3-litre aliquots of scandium-free sea-water and analysed by the procedure above. The recovery was assessed by counting a suitable aliquot of the solution before the oxine–butanol extraction, and quantitative results were obtained. Since the extraction efficiency was found to be consistently 98% at pH 1–4, no correction factor is required if samples and standards are carried through under the same conditions. The chemical recovery was tested by adding known amounts of scandium to 3-litre aliquots of scandium-free sea-water and carrying them through the complete process and was satisfactory (Table II).

TABLE II.—RECOVERY OF SCANDIUM

Sc(III) added, *μg*	Conc. of final solution, *ppm*	Conc. of Sc found, *ppm*	Chemical Recovery, %	Radiometric Recovery, %
~1				102
~1				99
~2				99
5	1	0·98	98	
5	1	0·99	99	
5	1	0·98	98	
10	2	2·01	100	
10	2	1·96	98	
10	2	1·93	97	
15	3	3·02	101	
15	3	2·94	98	
15	3	2·95	98	
20	4	4·04	101	
25	5	5·01	101	

(Sea-water sample 3 l. Final extraction volume 5 ml of 2·5% oxine in butanol)

Determinations made on two portions (80 and 100 l.) of a composite surface sample taken from the South China Sea showed that the scandium content was 0·01 ± 0·005 μg/l. The size of sample was determined by the very low scandium content, the final scandium concentration in the butanol solution being less than 0·5 μg/ml.

Storage of samples

Adsorption by containers is a serious source of error in analytical work dealing with constituents at sub-microgram levels. Radiometric techniques have been used to determine the loss of scandium due to adsorption by various types of containers. Sea-water (1 l.) which had been filtered through a 0·5-μ membrane was equilibrated with ^{46}Sc(III) as chloride, with 1 μg of carrier, and was pasteurized by heating twice to 80°. One series of samples was adjusted to the pH of natural sea-water (8·2) and the other to pH 2. Each of these series was stored in three types of sterilized containers: polyethylene, soda glass and pyrex glass. A standard was taken from each of these series and sealed in a counting tube for subsequent comparison work.

The samples were stored in the dark at room temperature. At weekly intervals, an aliquot was taken for scintillation counting against the standard. It was found that at pH 8, *ca.* 30% of the scandium was lost in the pyrex container, 15% in the polyethylene and 85% in the soda glass container. Absorption equilibrium was reached in the first week and no further loss took place. In the samples acidified to pH 2, no loss of scandium was observed over a period of six weeks. It is therefore recommended that the samples for scandium determination should be acidified to pH 2 at the time of collection and stored in any of the three types of container.

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Summary—A method for the determination of scandium in sea-water at the sub-microgram level has been developed. Scandium is coprecipitated with iron(III) hydroxide at pH 8–9, and then separated from the iron by ion-exchange. The final concentration is achieved by extracting the scandium into a solution of oxine in butanol. A nitrous oxide–acetylene flame is used for the determination by atomic-absorption spectroscopy. Recoveries of 99–100% are obtained. The storage of the solutions before analysis has been investigated by radiometric techniques with ^{46}Sc. The scandium concentration in surface waters of the South China Sea was found to be 0·01 ± 0·005 μg/l.

Zusammenfassung—Eine Methode zur Bestimmung von Scandium in Meerwasser im Submikrogrammbereich wurde entwickelt. Scandium wird bei pH 8–9 mit Eisen (III) hydroxid mitgefällt und dann vom Eisen durch Ionenaustauch getrennt. Endgültig angereichert wird das Scandium durch Extraktion in eine Lösung von Oxin in Butanol. Zur Bestimmung durch Atomabsorptionsspektrometrie wird eine Lachgas–Acetylen-Flamme verwendet. Man erhält Ausbeuten von 99–100%. Die Aufbewahrung der Lösungen vor der Analyse wurde radiometrisch mit ^{46}Sc überprüft. Die Scandiumkonzentration in Oberflächenwässern des Südchinesischen Meeres wurde zu 0,01±0,005 μg/l gefunden.

Résumé—On a élaboré une méthode pour le dosage du scandium dans l'eau de mer à l'échelle du submicrogramme. On coprécipite le scandium avec l'hydroxyde de fer(III) à pH 8–9, puis le sépare du fer par échange d'ions. La concentration finale est atteinte par extraction du scandium dans une solution d'oxine en butanol. On utilise une flamme protoxyde d'azote-acétylène pour le dosage par spectroscopie d'absorption atomique. On obtient des récupérations de 99–100%. On a étudié la conservation des solutions avant analyse par des techniques radiométriques avec le ^{46}Sc. On a trouvé que la concentration en scandium des eaux de surfaces de la mer de Chine du Sud est de 0,01 ± 0,005 μg/l.

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Determination of vanadium in ore samples by atomic-absorption spectrophotometry

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ATOMIC-ABSORPTION spectrophotometry has been used to determine minor constituents in a wide variety of materials at levels of a few ppm or even less, but very little has been published on its use for determination of vanadium.[1,2,3] The present paper discusses the avoidance of use of organic solvents (added to improve the sensitivity) and the elimination of iron and hydrochloric acid interference when an acetylene–nitrous oxide flame is used.

EXPERIMENTAL

Apparatus

Atomic absorption spectrophotometer, Model 303, with premix type burner with nitrous oxide head, vanadium hollow-cathode lamp and Digital Concentration Readout Accessory DCR-1 (all Perkin Elmer products).

Reagents

A 0·1% w/v stock solution of vanadium was prepared by dissolving 2·296 g of pure ammonium metavanadate in a litre of demineralized distilled water, and diluted to give a range of suitable standards. The isopropyl ether used was saturated with 8*M* hydrochloric acid. Ore samples were digested in hydrofluoric acid and in a reagent made of 200 ml of conc. nitric acid, 55 ml of conc. sulphuric acid and 20 ml of 85% phosphoric acid, mixed and diluted to 1 litre.

Instrument settings

The experimental working conditions were established in preliminary tests and are: wavelength 3184 Å; lamp current 35 mA; slit setting 4 (1 mm; 7 Å bandpass); scale expansion ×10; meter response setting 10; sample uptake 10 ml/min; flow-rates, N_2O 30 psi, 8 flow-meter divisions, C_2H_2 8 psi, 15 flow-meter divisions. The 3184 Å line under these conditions will detect a minimum vanadium concentration of 0·3 ppm.

RESULTS AND DISCUSSION

The type of flame giving maximum absorption was found by varying the acetylene flow and hence the height of the pink central zone of the flame. The results obtained with a 10-ppm vanadium solution are summarized in Table I.

TABLE I.—EFFECT OF HEIGHT OF CENTRAL FLAME ZONE ON THE ABSORPTION FOR A 10 PPM VANADIUM SOLUTION

Height of pink flame, *cm*	1	2	3	4	5
Absorption, %	11·0	28·4	36·5	29·0	17·7

A calibration curve for vanadium, with central zone height 3 cm, is linear up to 10 ppm.

One way to increase the absorption is to increase the proportion of free atoms by preventing the formation of VO.[3] This can be done by adding ions which compete for oxygen species in the flame. When aluminium chloride was added in increasing quantities the absorption increased, reaching a maximum when 200 ppm of aluminium had been added to a 10-ppm vanadium solution (Table II). Addition of 200 ppm of aluminium to all standards gave a steeper, but still linear, calibration curve up to 10 ppm of vanadium.

Because it was intended to develop a method for determining vanadium in copper and iron ore, the effect of these elements and of hydrochloric and sulphuric acids was investigated. Copper(II), hydrochloric acid and sulphuric acid did not interfere in concentrations up to 0·5*M*, 0·1*M* and 0·2*M* respectively, but iron(II) or (III) interfered at concentrations above 0·015*M*.

TABLE II.—EFFECT OF ALUMINIUM IONS ON THE ABSORPTION OF A 10-PPM VANADIUM SOLUTION

Al^{3+} added, *ppm*	0	50	100	200	300
Absorption, %	36·5	40·0	46·0	48·6	48·6

TABLE III.—DETERMINATION OF VANADIUM IN VARIOUS SAMPLES

Sample	Vanadium, %	
	Atomic-absorption	Colorimetry
1	0·61	0·63
2	0·40	0·39
3	0·22	0·24
4	0·11	0·10
5	0·27	0·25
6	0·86	0·89
7	0·68	0·66
8	0·31	0·33
NBS 61a (50·6% V)	50·4	50·5

It is therefore necessary to eliminate the iron interference, which is more marked when the vanadium content is low and a 5-g sample or more must be taken. This can be done by extracting iron(III) from 8*M* hydrochloric acid medium with isopropyl ether.[4] Because some vanadium is also extracted, the standard solutions must be treated in the same way, and because the high concentration of hydrochloric acid interferes, the solution, after extraction, must be evaporated to dryness and the residue dissolved in water (containing 0·5–1 ml of conc. sulphuric acid to prevent hydrolysis), and diluted to a known volume before measurement. The rate of sample uptake does not affect the results.

Several samples were analysed by atomic-absorption and by a colorimetric method,[5] yielding the results in Table III.

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Summary—An atomic-absorption method is described for the determination of vanadium in ores. With a nitrous oxide–acetylene flame and 200 ppm of Al^{3+} added to the sample, a sensitivity of 0·2 ppm for 1% absorption can be obtained. Iron above 0·015*M* interferes but can be extracted into isopropyl ether from 8*M* hydrochloric acid; the hydrochloric acid itself then interferes and must be removed by evaporation.

Résumé—On décrit une méthode d'absorption atomique pour le dosage du vanadium dans les minerais. Avec une flamme protoxyde d'azote–acétylène et l'addition de 200 ppm d'Al^{3+} à l'échantillon, on peut obtenir une sensibilité de 0,2 ppm pour 1% d'absorption. Le fer au-dessus de 0,015*M* gêne mais peut être extrait en éther isopropylique à partir d'acide chlorhydrique; l'acide chlorhydrique lui-même gêne alors et doit être éliminé par évaporation.

Zusammenfassung—Eine Atomabsorptionsmethode zur Bestimmung von Vanadium in Erzen wird beschrieben. Mit einer Lachgas-Acetylen-Flamme und Zugabe von 200 ppm Al^{3+} erhält man eine Empfindlichkeit von 0,2 ppm für 1% Absorption. Mehr Eisen als 0,015*M* stört, kann jedoch aus Salzsäure in Isopropyläther extrahiert werden; die verbleibende Salzsäure stört ihrerseits und muß durch Abdampfen entfernt werden.

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Determination of part-per-milliard concentrations of mercury by atomic-fluorescence flame spectrometry

(*Received* 5 *December* 1967; *Accepted* 31 *January* 1968)

THE determination of mercury is of considerable importance in clinical and toxicological investigations. The methods most widely employed in the determination of mercury are a colorimetric procedure using dithizone[1] and, more recently, atomic-absorption flame spectrometry.[2,3] The best detection limits for mercury have been reported by Lindström[4] who detected 0·001 ppm of mercury in aqueous solution by vaporizing the solution in the flame of a Beckman oxy-hydrogen burner, collecting the filtered vapour, and measuring the mercury content in a commercial mercury vapour meter. This paper reports the development of an atomic-fluorescence method for mercury which achieves comparable detection limits with savings in time and sample handling.

The atomic fluorescence technique has been described by Winefordner and Vickers.[5] The atomic fluorescence of mercury has been investigated previously by Winefordner and Staab[6] and Mansfield *et al.*[7] In these investigations a detection limit of 0·1 μg of mercury per ml was achieved by aspirating aqueous solutions directly into the flame above an integral aspirator-burner. In the present investigation a solvent extraction procedure has been used and the mercury aspirated in an organic solvent. The use of the solvent extraction procedure allows concentration of the mercury, increased aspiration rate, improved atomization efficiency and reduction of noise due to the scattering of exciting radiation by unvaporized solvent droplets.

EXPERIMENTAL

Apparatus

A Beckman model DU was used as the monochromator. The sample and photomultiplier compartments were replaced by a side-window photomultiplier housing with an 1P28 photomultiplier. The photomultiplier voltage and signal amplification were provided by a combination power supply/amplifier (Jarrell-Ash 26-780). The signal was read directly from the meter of the power supply/amplifier unit. The burner was of the integral-aspirator type (Jarrell-Ash 82-341 HETCO). The excitation source was a mercury pen light of the type used for wavelength calibration of spectrometers (Ultra Violet Products, Inc., San Gabriel, California). The pen light was enclosed in a metal box to reduce the intensity of radiation scattered into the monochromator. A single 1/2 × 1 in. opening in the box allowed illumination of the flame.

The arrangement of components is shown in Fig. 1. It was found that maximum fluorescence resulted when no lens was used in the exciting beam and the source was moved as close to the flame as the apparatus would permit (about 2 in.). Another source, a Phillips mercury vapour discharge lamp, was also tested, but the intensity of fluorescence was much less than that obtained with the pen light. The low fluorescence intensity seemed to be due to self-reversal of the mercury line at all currents for which a stable discharge could be maintained (0·2–0·9 A).

Reagents

The mercury stock solution was prepared by dissolving the appropriate weight of reagent grade mercuric chloride in demineralized water. Other mercury standards were prepared by dilution. Chloroform and isobutyl methyl ketone (IBMK) were used without further purification. Dithizone (diphenylthiocarbazone) solutions of concentration approximately 0·1% w/v were prepared in chloroform and IBMK. The solutions were filtered before use but otherwise were used without purification. Reagent grade acetic, hydrochloric and sulphuric acids were used.

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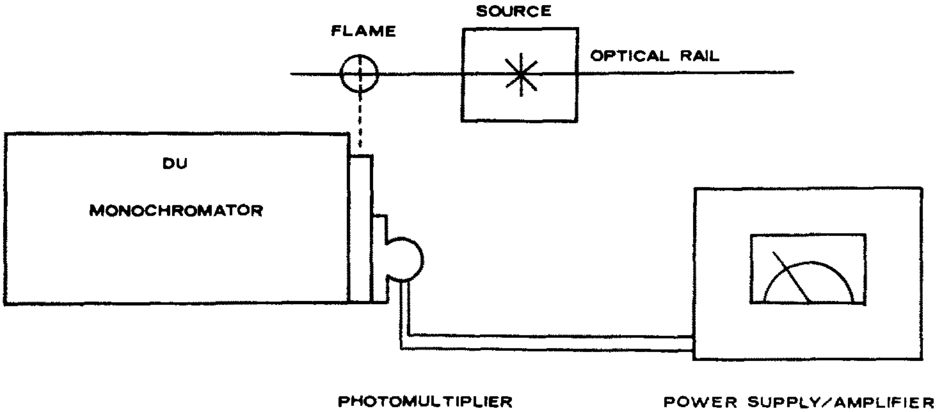

FIG. 1.—Arrangement of instrumental components.

Procedure

Extractions from aqueous solutions were made with dithizone in both chloroform and IBMK solution. Both solvents proved suitable for introduction into the flame, but very different flame conditions were required for the two solvents. The optimum experimental conditions are shown in Table I.

TABLE I.—OPTIMUM EXPERIMENTAL CONDITIONS FOR DETERMINATION OF MERCURY

	Chloroform	IBMK
Flow-rate, H_2, *l./min*	26·8	7·2
Flow-rate, O_2, *l./min*	8·8	6·5
*Flame height, *cm*	8	8

Spectral line 2537 Å; slit-width 2 mm.

* Measured from burner top to centre of entrance aperture.

The extraction was carried out as follows. To 100 ml of the mercury solution, brought to approximately pH 1 by addition of either concentrated hydrochloric acid or 1:1 0·5*M* sulphuric acid–0·5*M* acetic acid mixture, were added 2 ml of 0·1*M* dithizone solution in either chloroform or IBMK. The solution was thoroughly shaken and allowed to stand for 5–10 min and then the organic layer was collected in a 10-ml beaker and aspirated directly into the flame. No corrections were made for possible mutual solubility losses of the two layers. Such losses should be small and constant for the solvents employed, over the range of sample concentrations investigated. For a wider range of sample types where a variation in mutual solubilities might be expected, the organic layer should be diluted to known volume before aspiration.

With urine samples considerable emulsion formation occurred on shaking. No useful separation of the layers could be achieved with chloroform as solvent. With IBMK the layers were allowed to stand for about 10 min and the organic portion plus the layer of emulsion was then run into a 15-ml centrifuge tube. After centrifugation for 5 min the organic layer was withdrawn with a syringe, placed in a 10-ml beaker and aspirated into the flame.

Aqueous solutions containing 0·005, 0·01, 0·10, 1·00 and 5·00 μg of mercury per ml were extracted according to the procedure described and used to provide calibration curves. A blank treated in the same fashion as the sample was run with each sample measurement The blank allowed correction for the signal due to scattering of exciting radiation. Fluorescence signals reported are thus the result of pairs of blank–sample measurements. Blank corrections were only appreciable at the highest sensitivity setting (10^{-8} A full scale) used with the lowest sample concentrations.

RESULTS AND DISCUSSION

Calibration curves (log–log plots of meter reading *vs.* concentration) were straight lines of unit slope up to 5 μg/ml, the highest concentration measured, for both the chloroform and IBMK procedures. The chloroform extraction procedure gave the greater signal for a given concentration. At

1 μg/ml an average fluorescence signal of 178 divisions was obtained with the chloroform solution while the same concentration in IBMK gave a meter reading of 23 divisions. The limiting detectable concentration was approximately 0·002 μg/ml in either solvent. A standard deviation of 0·001 μg/ml was calculated for the blank–sample pair measurement of mercury in 8 solutions containing 0·005 μg of mercury per ml, the IBMK method being used. A standard deviation of 0·002 μg/ml was found for similar measurements with chloroform being used as solvent.

A brief study of the determination of mercury in urine indicated the feasibility of this determination *via* the IBMK extraction procedure. The results of a recovery study are shown in Table II. No mercury was detected in several urine specimens which were examined without added mercury. This method should provide a very rapid and sensitive means of screening urine samples for mercury content.

TABLE II.—RECOVERY OF MERCURY ADDED TO URINE

Added, *μg/ml*	Recovered, *μg/ml*
0·10	0·10
0·10	0·08
1·0	1·2
1·0	0·8
1·0	0·9
1·0	0·9

Atomic-fluorescence also provides a convenient, highly sensitive means for the determination of organic-bound mercury without prior decomposition of the organic species. The usefulness of the atomic-fluorescence technique for analyses of this type was demonstrated during the course of this investigation by a problem presented to us in which an organomercury intermediate was suspected of being formed during a reduction at a mercury cathode. A sample was withdrawn from the electrolysis cell and fractionated by thin-layer chromatography, then the fractions were extracted into chloroform and tested for mercury by direct aspiration of the chloroform solutions into the flame. The occurrence of mercury in one of the fractions was quickly established.

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Summary—A method is reported for the determination of mercury in the range 0·002–1 μg/ml. Mercury is extracted by dithizone from aqueous solutions into chloroform or isobutyl methyl ketone, the organic solution is aspirated into a hydrogen–oxygen flame, and the intensity of atomic-fluorescence of mercury is measured. The method should be particularly useful for the determination of mercury in urine and for the determination of organic-bound mercury without prior decomposition.

Résumé—On décrit une méthode de dosage du mercure dans le domaine 0,002—1 μg/ml. Dans cette méthode, on extrait le mercure en chloroforme ou isobutyl méthylcétone au moyen de dithizone à partir de solutions aqueuses, la solution organique est aspirée dans une flamme hydrogène–oxygène et l'on mesure l'intensité de la fluorescence atomique du mercure. La méthode devrait être particulièrement utile pour le dosage du mercure dans l'urine et pour le dosage du mercure lié organiquement sans décomposition préalable.

Zusammenfassung—Eine Methode zur Bestimmung von Quecksilber im Bereich 0,002–1 μg/ml wird angegeben. Dabei wird Quecksilber mit Dithizon aus wäßrigen Lösungen in Chloroform oder Isobutylmethylketon extrahiert, die organische Lösung in eine Wasserstoff—Sauerstoff–Flame gesaugt und die Intensität der Atomfluoreszenz von Quecksilber gemessen. Die Methode sollte besonders bei der Bestimmung von Quecksilber in Urin nützlich sein und bei der Bestimmung organisch gebundenen Quecksilbers ohne vorhergehende Zersetzung.

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ANNOTATION

Properties of zirconium compounds likely to be of interest to the analytical chemist

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A FEW generations ago, chemists commonly regarded nearly all compounds of metals with acid radicals as salts. "Salts" containing multivalent metals were thought to differ from those containing univalent metals, mainly in the coulombic effects associated with the charge on the metal atom. A few rules of thumb were developed from this concept, and their utility entrenched the idea. For example, uni-univalent salts were categorized as most highly ionized, uni-bivalent and bi-univalent not quite so highly ionized, and multi-multivalent salts least ionized. This trend was supposed to reflect the increased resistance of ions of high charge to separation. By extension, it was inferred that the less ionized salts were less likely to be soluble in polar ionizing solvents such as water. The inference appeared confirmed by the considerable water-solubility of most uni-univalent salts, such as the alkali halides, and the frequent insolubility of "salts" of multivalent ions, such as calcium phosphate, aluminium arsenate, or zirconium silicate.

These views have undergone considerable alteration. Pauling's principle of electroneutrality[1] taught that in stable compounds the atoms do not carry charges greater than ± 1. Later studies have confirmed this;[2] even the most extremely polar binary compound, caesium fluoride, has about 7% covalent bonding. It follows that compounds of bivalent and multivalent elements must be largely covalent in character. The structures of these compounds show evidence of bonding substantially similar to that of organic compounds. Inorganic compounds of multivalent elements are often characterized by certain polarization phenomena, which we shall discuss, but these are not grossly different in kind from the polarization phenomena found in many organic compounds, such as amino-acids and proteins. Indeed, a great deal of the chemistry of metallic elements may be described in terms of organic chemistry. The present presentation is limited to zirconium compounds, especially to those aspects likely to be of interest in analytical chemistry.

CATIONS CONTAINING ZIRCONIUM

At ordinary and moderately elevated temperatures, there is no evidence that a monatomic zirconium cation, Zr^{4+}, Zr^{3+}, or Zr^{2+} exists as a separate entity, or that such ions are units that are redistributed as such during the reactions of zirconium compounds. The zirconium atom is usually part of a polyatomic complex. In complexes, the zirconium atom almost always has a negative formal charge, and may be truly electronegative. Studies of interstitial compounds of zirconium with carbon, oxygen and nitrogen have led to the conclusion that the zirconium atom bears a negative charge in these compounds.[3,4]

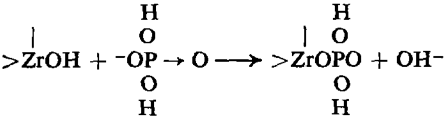
In the usual analytical circumstances, *i.e.*, in aqueous solution, zirconium is nearly always bonded to water or to the species derived from it, hydroxide or oxide*, and in nearly all the reactions induced in aqueous media an oxygen atom is displaced from the zirconium–oxygen species by forming a stronger bond with the reactive species to take the place of the previously existing bond. This can be done in two ways. (*a*) The oxygen atom can be successively protonated

$$>\mathrm{Zr}=\mathrm{O} \xrightarrow{\mathrm{H}^+} >\overset{|}{\mathrm{Zr}}\mathrm{OH} \xrightarrow{\mathrm{H}^+} >\overset{|}{\underset{|}{\mathrm{Zr}}}\leftarrow \mathrm{OH_2} \xrightarrow{\mathrm{H}^+} >\overset{|}{\underset{|}{\mathrm{Zr}}}\leftarrow \mathrm{OH_3}^+.$$

---

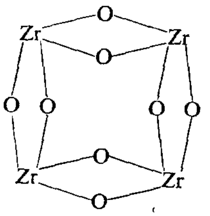
* Exceptions include ZrF_7^{-3} and ZrF_8^{-4} at pH < 4·0 in fluoride-containing systems; $ZrCl_6^{-2}$ and $Zr(CNS)_6^{-2}$ in extremely acidic solutions.

The more acidic the environment, the more highly protonated is an oxygen atom bound to zirconium and the weaker the bond. In very strongly acidic solution, the hydronium ligand can be displaced by chloride with the formation of chlorozirconate,[5] whereas in ordinary zirconyl chloride solutions, no chlorine is bonded to zirconium.[6] (*b*) An agent may be used which offers the zirconium a highly basic oxygen atom, such as that in a phosphate ion:



$$>\mathrm{ZrOH} + {}^{-}\mathrm{O}\underset{\underset{\mathrm{H}}{\mathrm{O}}}{\overset{\overset{\mathrm{H}}{\mathrm{O}}}{\mathrm{P}}} \rightarrow \mathrm{O} \longrightarrow >\mathrm{ZrO}\underset{\underset{\mathrm{H}}{\mathrm{O}}}{\overset{\overset{\mathrm{H}}{\mathrm{O}}}{\mathrm{P}}}\mathrm{O} + \mathrm{OH}^{-}$$

Those zirconium compounds in which the zirconium has been found to occur in a cation are generally protonated forms of zirconium oxide. Zirconyl chloride, $ZrOCl_2 . xH_2O$, is a typical example. The core structure of the zirconium species is



where the zirconium atoms are in a plane, and in each pair of oxygen atoms one is above and one below the plane.

The core is electrically neutral but acts as a Lewis base, accepting protons and acquiring a positive charge to become $4ZrO_2 . yH^+$ and form salts $[4ZrO_2 . yH^+]\, zA^-$, where z is variable and A represents a group of atoms of net charge -1. In aqueous solutions of zirconyl chloride and bromide, halide ions are held by coulombic forces at the middle of each side of the square formed by the zirconium atoms.[6] Only in the cystalline zirconyl halides do we have direct evidence of two halide ions per zirconium atom in the unit structure. In some of the recent literature, the name zirconyl chloride has been replaced by zirconium oxide chloride, which is justified by the structure.

The zirconium species in an aqueous solution of zirconium oxide chloride can be represented:

$$[4ZrO_2{\cdot}xH_2O{\cdot}yH^+{\cdot}zCl^-]^{y-z}.$$

The quantity $y - z$ is usually positive, and the species is a complex zirconium oxide-containing cation. Its charge and composition will vary with changes in the environment. The value of x will tend to bring the co-ordination number of the zirconium atoms to eight. It is possible to regard such a system as a solution of zirconium oxide made possible by stabilization of Zr_4O_8 oligomers by electrostatic repulsion, so preventing the development of macromolecular crystalline zirconium oxide.

There are two methods for simple gravimetric determination of zirconium in such a solution (*a*). To neutralize the charge on the species and cause its flocculation:

$$4ZrO_2{\cdot}xH_2O{\cdot}yH^+.zCl^- + yOH^- \longrightarrow 4ZrO_2{\cdot}x'H_2O{\cdot}z'Cl^- + (z - z')\,Cl^- + (y + x - x')\,H_2O.$$

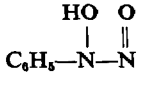
The precipitate is commonly called hydrous zirconia. It forms as micelles about 50 Å in diameter, as determined by electron micrography. There is no evidence of crystal structure, but digestion at the boil under suitable conditions will develop either the cubic or monoclinic crystal lattices.[7] When first precipitated, the micelles contain small amounts of tightly held halogen, z' being about 1 at pH ~ 4, and zero at pH 9. Some investigators have been disposed to treat the product containing one chloride ion per four zirconium atoms as a definite compound.[8] This suggests the possibility of a clathrate structure, in which the chloride ion occupies the interior of the square. Regardless of the values of x' and z' in the precipitate, calcination at about 1000° leaves a residue of ZrO_2.

(*b*) The zirconia may be precipitated by an oxy-anion with a greater affinity for the zirconium atom than the oxy-ligands already bound to the zirconium. Some such anions (*e.g.*, phosphate and mandelate) form molecular aggregates with zirconium that separate from solution and are useful for analysis. Others (*e.g.*, acetate and under some conditions sulphate) form charged species which remain dispersed and are not suitable for analytical application.

$$ZrO_2{\cdot}xH_2O + 2H_3PO_4 \longrightarrow Zr(HPO_4)_2{\cdot}yH_2O \xrightarrow{\text{heat}} ZrP_2O_7$$

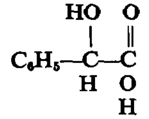
$$ZrO_2{\cdot}xH_2O + 4C_6H_5CHOHCO_2H \longrightarrow Zr(C_6H_5CHOCO_2)_4H_4 \xrightarrow{\text{heat}} ZrO_2.$$

Many other precipitants have been used, particularly arsenic acid and some of its organic derivatives, aryl carboxylates, sulphonated dyes, and periodic acid.[9] Cupferron, which bears a structural relationship to mandelic acid:



$C_6H_5{-}N(OH){-}N{=}O$

Cupferron



$C_6H_5{-}CH(OH){-}C(=O)OH$

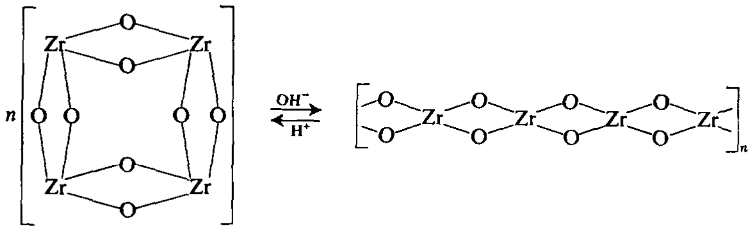
Mandelic acid

precipitates zirconium quantitatively from 20% sulphuric acid. The only precipitate of zirconium in which zirconium is not bound to oxygen and which has found some use in zirconium analysis is the fluorozirconate, $BaZrF_6$.[10]

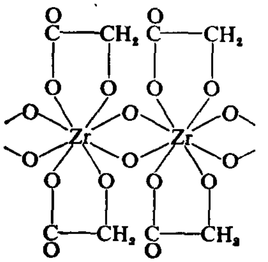
It is not feasible, and is probably impossible, to electro-deposit zirconium from aqueous medium.

ANIONS CONTAINING ZIRCONIUM

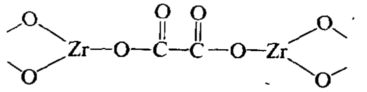
The tetrameric zirconium oxide skeleton of zirconium oxide chloride in aqueous solution is labile and convertible into other forms, and by forming adducts with suitable anions yields complex zirconium-containing anions. If the acidity of the environment is reduced, the ring structure appears to alter to a chain structure:



This change is surmised from the following observations: (*a*) after partial neutralization and evaporation to dryness of a zirconium oxide chloride solution, no crystalline products are obtained, but only glassy residues that appear amorphous on X-ray examination; (*b*) syrupy and jellied structures are obtained from hydrolysed derivatives of zirconium oxide chloride.[11] The cationic characteristics of the zirconium species largely or completely disappear with the formation of the polymer chain species. Under conditions of mild acidity, neutrality, or alkalinity, anions tend to form co-ordinate bonds with the zirconium atoms of the chains to give structures of the diglycollatozirconate type:



or to give intercalation complexes of the oxalatozirconate[12] type:



Such chains may contain substoichiometric proportions of anions, and these compounds are apt to be unsuitable for analytical determinations. Pilkington and Wilson concluded that prolonged boiling of zirconium solutions with at least 5*N* sulphuric acid is necessary to ensure depolymerization of zirconium species and to obtain a solution suitable for titration with EDTA.[13]

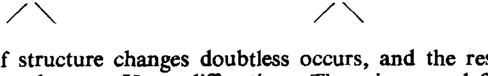
Treatment of zirconium oxide chloride solutions with various acids under described conditions gives the following series of complex acids, in which zirconium occurs as part of a complex anion: $H_2ZrO(SO_4)_2{\cdot}3H_2O$, $H_4Zr(C_2O_4)_4$, H_2ZrF_6, $H_3ZrOH(O_2CCH_2O)_3$. The last of these, triglycollatozirconic acid, is only sparingly soluble in water, but forms very soluble alkali salts. The complex carbonate, $(NH_4)_3ZrOH(CO_3)_3{\cdot}2H_2O$, can be formed directly by the action of ammonium bicarbonate on a number of zirconia-containing materials.[14] These complexing anions have the following significant consequences for analysis. (*a*) They may act as masking agents; *e.g.*, moderate concentrations of sulphuric acid inhibit the precipitation of zirconium tetramandelate, but not of zirconium phosphate. (*b*) They may provide means of dissolving precipitated zirconium compounds; *e.g.*, the very insoluble zirconium phosphate (diphosphatozirconic acid) can be dissolved with hydrofluoric acid or with potassium carbonate solution. (*c*) They can be adapted to serve as the basis of analytical procedures, *e.g.*, the characteristic colour of the alizarin–zirconium complex disappears when enough fluoride is added, and this provides a means of determining fluoride.[15] (*d*) Anionic complexes of zirconium precipitate certain substances whereas the cationic complexes do not; notably, amino-acids such as glutamic and aspartic acid are precipitated by disulphatozirconic acid ("zirconium sulphate"); diacetatozirconic acid and disulphatozirconic acid react with and tan collagen; such possibilities for the determination of amino-acids and proteins appear attractive.

Certain adducts of zirconium, such as those with flavones and flavianic acid, have characteristic absorption and/or fluorescence spectra suitable for analytical determinations.[16,17] Many dyes have been shown useful for photometric determination of zirconium, notably Alizarin S, Xylenol Orange, Galleinphthalein, Pyrocatechol Violet, Methylthymol Blue, Solochrome Violet R, Arsenazo III, Eriochrome Cyanine R, Chrome Azurol S, Neothorin, anabasine, and derivatives of chromotropic acid.

ZIRCONIUM COMPOUNDS AND ION-EXCHANGE

The polymeric structures of many zirconium compounds give them properties similar to those of organic polymers. While the solids tend to be more rigid than those of their organic counterparts, this can sometimes be overcome by the use of plasticizers. For example, films of glyceratozirconium chloride[11] plasticized with glycerine are quite flexible and look like films of Teflon. Those polymers, of which there are quite a few examples, which contain replaceable protons or alkali metal ions, show ion-exchange properties that are similar to those of the organic ion-exchange resins.

When a phosphate is added to an acidic solution of a zirconium salt, an average of about two phosphato ligands complex the zirconium atom:



$$\mathrm{Zr} + 2H_2PO_4^- \longrightarrow {}^-H_2PO_4 \rightarrow \mathrm{Zr} \leftarrow O_4PH_2^-.$$

A complex sequence of structure changes doubtless occurs, and the result is a gelatinous white precipitate which is amorphous to X-ray diffraction. There is an undefined polymer structure in which there are replaceable protons on the phosphato ligands. The precipitate is designated diphosphatozirconic acid. Alberti and Grassini have reported that filter paper impregnated with this precipitate can be used to separate 26 cations.[18] Alberti and a number of collaborators subsequently reported at length on the ion-exchange properties of diphosphatozirconic acid, and notably on the effects on the exchange capacity for Tl, Cs, Rb, K, Na, Li, Ba, and Sr when it was dried at various temperatures.[19]

Clearfield and Stynes discovered that long digestion of the gelatinous phosphate in certain acid media develops a crystalline structure of empirical composition $Zr(HO_4P)_2{\cdot}H_2O$. It contains one replaceable hydrogen atom per phosphate group. The crystalline phosphate is a good exchanger for alkali metal ions other than caesium, whereas the gelatinous phosphate has a high capacity for caesium.[20] The crystalline phosphate is more resistant to hydrolysis than the gelatinous one.

Other zirconium compounds with ion-exchange capabilities include hydrous zirconia, zirconium molybdate, zirconium tungstate, and zirconium ferrocyanide. The ferrocyanide holds particular promise for the absorption and separation of the higher atomic weight alkali metals, including caesium.[21]

MISCELLANEOUS

Zircon ($ZrO_2 \cdot SiO_2$) and zirconia can be fabricated into crucibles suitable for use at well over 1000°. Zirconium metal crucibles have proved to have outstanding durability for use with alkali peroxide sinters, and are commonly found to survive 150 or more firings. Zirconium metal sponge is a powerful getter and is useful in removing last traces of oxygen, nitrogen, and carbon from sweep gases.

Precipitated zirconia (hydrous zirconia) can be used to remove trace impurities from water. It will lower the concentration of dissolved silica or alkylbenzene sulphonate to about 1 ppm.

Zirconium(IV) is an extremely stable oxidation state, and unlike titanium(IV) or cerium(IV), it cannot interfere in oxidimetry. Zirconium oxide, doped with an oxide of a metal of lower valence, is a good anionic conductor at elevated temperatures. A number of devices depending on this property have been described for use in measuring the oxygen potential of melts, in the range 700–1600°.[22]

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Summary—A review of zirconium chemistry, with emphasis on the features underlying the chemical methods of determining this element, and an application of zirconium compounds in the analytical chemistry of other species.

Zusammenfassung—Eine Übersicht über die Zirkonchemie mit besonderem Nachdruck auf den Eigenschaften, die den chemischen Analysenmethoden für dieses Element zugrunde liegen, und auf der Anwendung von Zirkonverbindungen in der analytischen Chemie anderer Stoffe.

Résumé—Une revue de la chimie du zirconium, en mettant l'accent sur les caractères qui sont à la base des méthodes chimiques de dosage de cet élément, et sur l'emploi de composés du zirconium dans la chimie analytique d'autres espèces.

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PRELIMINARY COMMUNICATION

On the possibility of using an electromagnetic radioisotope separator in conjunction with charged-particle and photon-activation analysis

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During the past few years activation analysis with charged particles and photons has shown great promise as a highly sensitive method for the measurement of the light elements at the microgram and sub-microgram level.[1-6] However, the use of this analytical tool to its full potential is limited for several reasons: (*a*) in many cases non-destructive techniques cannot reach ultimate sensitivity and accuracy because of interfering activities from matrix material or other highly active impurities present in the sample, (*b*) chemical separation techniques are restricted by the time factor, that is, separation of a large number of trace elements would require a time excessive in comparison with the half-lives of the isotopes produced by the activation, (*c*) to reach the highest sensitivity, high-efficiency beta-counting will in many cases be considered, requiring the radioisotopes to be recovered in such a way that self-absorption effects are minimized.

The need for radiochemical separations after use of these activation techniques has been shown by several authors. Albert,[1] Engelmann,[4] and Baker[6] have developed separation methods, but these are generally restricted to the recovery of one radioisotope. Further developments in techniques for obtaining radiochemically pure radioisotopes is necessary, with improvements in selectivity, speed, number of trace elements recovered ("multi-element analysis") and recovery of the isolated radioisotope in a form suitable for beta-counting.

As a new approach toward these objectives a study has been started on the use of electromagnetic separation of the radioisotopes present in an activated sample. The isotope separator used in this preliminary study is a small device built at the University of Colorado. A detailed description of this machine has been given elsewhere by Wahlin.[7] From reference data[8] and preliminary experiments, the analytical potential of electromagnetic radioisotope separation coupled with nuclear activation-analysis can be evaluated as follows.

The selectivity can be derived from the dispersion, D, which is the distance, on the collecting sheet, between two species of masses M and $M + \Delta M$, and is given by $D = d/M$ where d is a function of E/V, E being the field-strength (in V/cm) between the electric deflection plates, and V the accelerating voltage. The extreme cases of maximum and minimum dispersion may be illustrated for the case of light isotopes, taking $M = 16$, $\Delta M = 1$, and d variable from 0 to 160 cm. Maximum dispersion is obtained for $d = 160$ cm: $D_{\max} = 10$ cm. Minimum dispersion will be given by $D_{\min} = b$, where b is the half-width of the mass-peak M. Experience with the electromagnetic separator has shown that $b = 0{\cdot}2$ cm. Thus, D can be adjusted to allow the collection of a narrow or wide mass-range on the collecting sheet, which is approximately 20 cm in length.

Speed is another feature worth mentioning. The length of separation time needed to give the maximum activity of the collected sample will depend upon the half-lives of the radioisotopes considered. It can be shown[9] that the amount of activity A_t collected after a separation time t, for a radioisotope having a decay constant λ, is

$$A_t = A_0 \cdot t \cdot e^{-\lambda t}$$

where A_0 is the number of radioactive atoms present at time zero. The maximum activity collected is obtained for a separation time $t = 1/\lambda = 1{\cdot}44 \times t_{\frac{1}{2}}$ ($t_{\frac{1}{2}}$ = half-life of the radioisotope considered). It must be noted further that for $t = 0{\cdot}7\, t_{\frac{1}{2}}$, $\sim$80% of the maximum activity is already obtained. In charged-particle and photon-activation where most of the radioisotopes belonging to the light elements have half-lives of less than 2 hr, the separation time would therefore be in the minute–hours range.

The efficiency of electromagnetic separations usually varies between 5 and 15% and is therefore lower than the efficiency obtainable with most chemical separation techniques. However, this lower yield is still acceptable on account of the speed of separation and the fact that the radioisotopes collected can be counted with practically no self-absorption, so that beta-counting can be used when highest detection efficiency is necessary. Quantitatively the material collected for a given ion-current in a radioisotope separator can be expressed[10] as $m = kti$ where m is the number of microgram-atoms of separated isotope (convertible into sample weight by multiplication with the mass number), i is the ion-current in μA, t the time taken for separation (in hr), and k is a constant depending on the characteristics of the separator ($k \sim 0{\cdot}3$ for the Colorado machine "Colutron"). Because the ion-current is limited (up to 25 μA per isotope in our case) and since only the ions belonging to the trace elements are of interest, the experimental conditions are best when the separator does not need to handle the matrix material itself. This can be achieved either by letting the impurities boil off from the sample at a temperature kept below the volatilization point of the matrix or by removing the bulk sample material chemically and then separating the impurities remaining. (In the latter case carriers can be added to prevent losses of the trace elements during the removal of the bulk material.)

In the preliminary experiments, for practical reasons, we used mixtures (in powder form) of long-lived radioisotopes produced by thermal neutron activation. The first separations were run for short time intervals (less than 30 min) at low ion-currents on samples composed of activated cadmium (mainly ^{115m}Cd) in an iron matrix. Recovery obtained was low (up to 5%), but it seems that this yield can be increased by a factor of 2 or 3 without major difficulties. Then the selectivity was tested under extreme conditions at a low dispersion set to separate the mass range 3–200 on a 20-cm collection sheet. The mixtures to be separated contained the following radioisotopes: ^{24}Na, ^{45}Ca, ^{65}Zn, ^{75}Se, ^{115m}Cd, ^{117}Sn, ^{134}Cs, ^{197}Hg. The chemical composition of the components was chosen in such a way that the ions produced at a working temperature of 1700° in the ion source would be in elemental form. The isotopes recovered on separate spots on the collecting sheet were checked for purity by means of their gamma-spectra and half-lives. All the radioisotopes present could be identified, except ^{117}Sn. Apparently ^{117}Sn was masked by ^{115m}Cd and its daughter ^{115}In which have much higher specific activities. Further, the spot of the collected ^{197}Hg was broader than expected. This may be due to the fact that in separation of more than one element at the same time there are problems due to differences in vapour pressures and ionization efficiencies. From these preliminary experiments we could establish that even at low dispersion satisfactory selectivity can be obtained over a wide mass-range. However, extensive experimental studies are needed to develop this separation technique and assess its full possibilities. Improvement and reproducibility of the separation efficiency and optimum design of an ion source are among the most important questions to be studied.

This proposed use of charged-particle and photon-activation analysis coupled with an electromagnetic radioisotope separator opens challenging possibilities for the simultaneous determination of a whole range of traces of light elements at the sub-microgram level. It is clear that the application of a radioisotope separator is not limited to charged-particle and photon-activation analysis, but also appears interesting as a tool to be used with neutron-activation analysis.

Acknowledgments—I would like to express my appreciation to Professor R. E. Wainerdi and the members of this Laboratory for many stimulating discussions. Thanks are also due to Lars Wahlin, University of Colorado, for his advice and helpful suggestions as well as for running the samples. I am indebted to the Nuclear Physics Laboratory, University of Colorado for permitting the use of the "Colutron". The work was supported by NASA Grant NsG 239-62.

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Summary—A proposal is made for the use of electromagnetic radioisotope separation following charged particle, photon- or neutron-activation. Features of this separation technique are speed and selectivity, opening new possibilities for simultaneous determination of several trace elements, especially the light ones. Preliminary experiments have shown the possibilities if this separation technique is used in conjunction with activation analysis.

Zusammenfassung—Eine elektromagnetische Radioisotopentrennung nach vorangegangener Aktivierung mit geladenen Teilchen, Photonen oder Neutronen wird vorgeschlagen. Wesentliche Eigenschaften der neuen Methode sind Schnelligkeit und Selektivität, was neue Moglichkeiten zur gleichzeitigen Bestimmung mehrerer, besonders leichter Spurenelemente eröffnet. Vorläufige Versuche zeigten gute Möglichkeiten bei Verwendung dieser Trennmethode zusammen mit der Aktivierungsanalyse auf.

Résumé—On propose l'emploi d'une séparation électromagnétique des radioisotopique suivant une activation par particules chargées, photons ou neutrons. Les caractères de cette technique de séparation sont la rapidité et la sélectivité, ouvrant de nouvelles possibilités pour les dosages simultanés de plusieurs éléments à l'état de traces, spécialement les éléments légers. Des expériences préliminaires ont montré les possibilités de cette technique de séparation utilisée en liaison avec l'analyse par activation.

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EXTRACTION OF METALS FROM METAL ION-CATECHOL-QUATERNARY BASE SYSTEMS

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Summary—Methods are given for the extraction of iron(III), molybdenum(VI), titanium(IV), niobium(V), vanadium(IV), uranium(VI) and tungsten(VI) as ternary complexes with catechol and a quaternary cation such as n-butyltriphenylphosphonium, n-propyltriphenylphosphonium, tetraphenylarsonium, cetylpyridinium, cetyltrimethylammonium and 2,3,5-triphenyltetrazolium, the solvent being chloroform. By use of masking agents and pH control, some of these elements can be separated from each other by this means.

CATECHOL is a rather non-selective reagent which gives strongly coloured chelates with iron(III), vanadium(IV), niobium(V), titanium(IV), molybdenum(VI), tungsten(VI), cerium(IV) and uranium(VI) in aqueous solution.[1] Some metal chelates of catechol can be directly extracted into polar solvents such as aliphatic alcohols or ketones.[2] The partition coefficient is sometimes considerably increased if the extraction is carried out in the presence of an organic base. In such cases ion-association complexes are usually formed, consisting of an anionic metal chelate associated with an organophilic cation of a base, as was shown earlier for the catechol chelates of molybdenum(VI) in the presence of pyridine,[3] titanium(IV) in the presence of *N*-heterocyclic bases,[4] diantipyrilmethane,[5] antipyrine,[6] α,α′-dipyridyl,[7] *N*-acetylanabasine,[8] tetraphenylarsonium chloride[9] and other bases,[10,11] and vanadium(IV) in the presence of diphenylguanidine.[12]

In this paper we report studies on the extraction into chloroform of metal ions such as iron(III), molybdenum(VI), titanium(IV), niobium(V), vanadium(IV), uranium(VI) and tungsten(VI) from aqueous solutions containing excess of catechol and various quaternary salts such as n-butyltriphenylphosphonium bromide (BTPP), n-propyltriphenylphosphonium bromide (PTPP), tetraphenylarsonium chloride (TPA), cetylpyridinium bromide (CP), cetyltrimethylammonium bromide (CTMA) and 2,3,5-triphenyltetrazolium chloride (TTC).

For TPA the extraction is usually limited to a narrow pH range, and CP and CTMA have considerable detergent properties which complicate the separation of phases during the extraction. TTC is easily reduced at pH >4 to interfering coloured formazans which are also extracted. Only BTPP and PTPP are found to be good extracting agents, and so this paper contains results for these reagents only.

The nature of the various ion-association complexes extracted will be the object of further studies.

EXPERIMENTAL

Reagents

Reagents were commercial products, purified where necessary. Stock solutions were standardized by the usual methods.

Procedure

Equal volumes (10 ml) of aqueous solution and chloroform were shaken for 15 min in 50-ml separating funnels. The acidity of the aqueous phase was adjusted beforehand with dilute sulphuric acid or ammonia, or acids of known concentration. This period of 15 min was always found sufficient for equilibration.

Adherence of the organic phase to the Lambert-Beer law was examined under the optimum conditions for particular systems. The apparent molar absorptivity ε was evaluated from the slope of the linear plot of absorbance against metal ion concentration in the aqueous phase, by regression analysis,[14] which also gives the standard deviation of ε and the absorbance of the blank A_0.

The 95% confidence interval μ for the practical determination of a particular metal was obtained from[13] $\mu = \pm ts/\sqrt{n}$ where s = standard deviation of the mean of n measurements and t = Student's t for $n - 1$ degrees of freedom.

RESULTS

Vanadium(IV)

A blue species is extracted at pH $\geqslant$ 1·6 from solutions containing 0·4*M* catechol and 0·01*M* BTPP and has λ_{max} 618 and 904 mμ. The maximum extraction is reached at pH 2·4–2·7 under these conditions. This pH range is shifted to pH 2·8–3·6 for 0·1*M* catechol, and the absorbance of the chloroform layer rapidly decreases with the further decrease in catechol concentration (Fig. 1). The blue hue of the chloroform layer changes to blue-green after 10 min but this involves only an absorbance increase at 380 mμ. The Lambert-Beer law is obeyed for 0·1–6 ppm of vanadium at 620, 930 and 1050 mμ in the presence of 0·1*M* catechol excess and 0·01*M* BTPP in the aqueous layer; $\varepsilon = (11{\cdot}14 \pm 0{\cdot}08) \times 10^3$ and the sensitivity limit is 0·02 μg/cm^2 for A = 0·01 at 620 mμ, in pure solutions. Formate, sulphate and chloride, even in large excess, do not interfere.

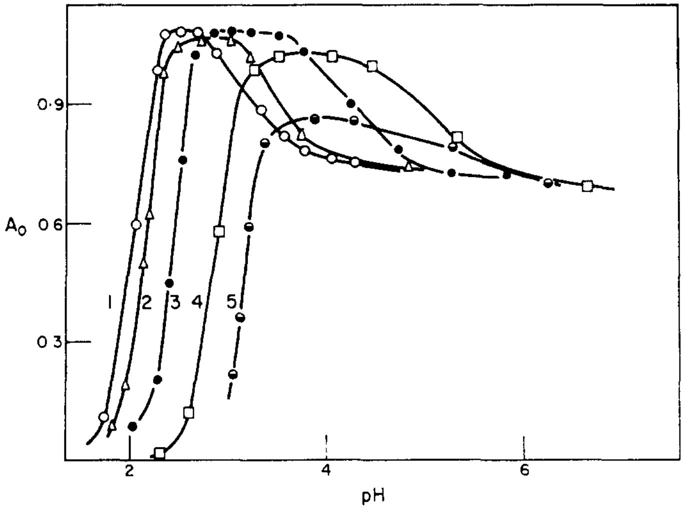

FIG. 1.—pH-Absorbance curves for the system V(IV)–catechol–BTPP.
λ = 620 mμ; $c_M = 1{\cdot}0 \times 10^{-4}M$; c_B = 0·005*M*.
c_R: *1*—0·4*M*; *2*—0·2*M*; *3*—0·1*M*; *4*—0·05*M*; *5*—0·02*M*.

Determination of vanadium(IV) in the presence of titanium(IV), molybdenum(VI), iron(III) and uranium(VI). To the slightly acid solution of the sample, containing 1–60 μg of vanadium(IV) as sulphate, add 1 ml of 1*M* catechol solution, adjust to pH 2·9–3·3 with dilute ammonia, and add 1 ml of 0·1*M* formate buffer (pH 3·2) and 1 ml of 0·05*M* BTPP. Dilute to 10 ml and extract with

10 ml of chloroform. Measure the absorbance of the organic layer at 620, 930 or 1050 mμ. At these wavelengths ε is (11·14 ± 0·08) × 10^3, (7·76 ± 0·17) × 10^3 and (5·61 ± 0·15) × 10^3 respectively. If only uranium is present besides vanadium measure at 930 mμ. In the presence of not more than twice as much molybdenum as vanadium, measure at 1050 mμ. At these wavelengths the absorbance is not influenced by the slight increase with time of the absorbance at 380 mμ. Tungsten interferes.

TABLE I.—DETERMINATION OF VANADIUM(IV)

Vanadium(IV)				Other ion present,
Taken, *ppm*	Found, *ppm*	$t.s/\sqrt{n}$, *ppm*	*n*	*ppm*
5·09	5·12	±0·04	15	—
	5·19	±0·05	5	Ti(IV) 47·9
	5·19	±0·05	4	Ti(IV) 4·8
	5·28	±0·10	4	Mo(VI) 95·9
	5·10	±0·10	5	Fe(III) 83·8

Titanium(IV)

A yellow association complex, with λ_{max} 370 mμ,[15] begins to be extracted at pH 0·5 from solutions containing 0·4*M* catechol and 0·005*M* BTPP. The pH of maximum extraction is 1·6 but this value is shifted to considerably higher pH if the concentration of catechol is decreased. Several ion-association complexes of the titanium–catechol chelate are formed, depending on the pH and the concentration of catechol, and these influence the shape of the pH-absorbance plots (Fig. 2).[15]

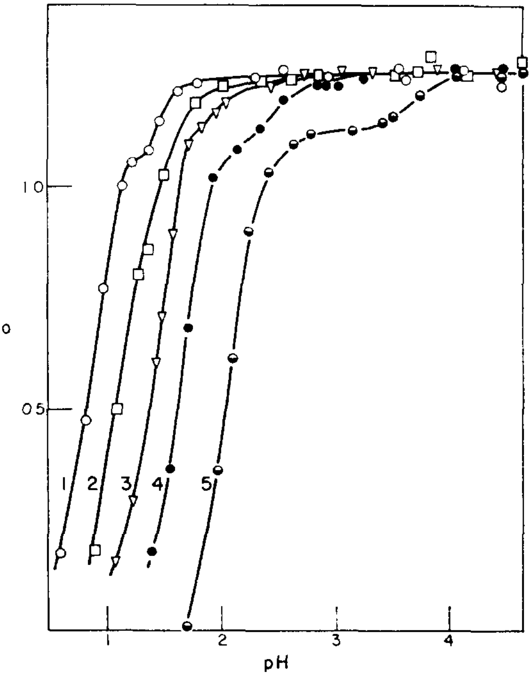

FIG. 2.—pH-Absorbance curves for the system Ti(IV)–catechol–BTPP.
λ = 380 mμ; c_M = 1·0 × 10^{-4}*M*; c_B = 0·005*M*.
c_R: *1*—0·4*M*; *2*—0·2*M*; *3*—0·1*M*; *4*—0·05*M*; *5*—0·02*M*.

Beer's law is obeyed for 0·3–6 ppm of titanium at 410 mμ; $\varepsilon = (9{\cdot}88 \pm 0{\cdot}16) \times 10^3$. At this wavelength any oxidation products of catechol which may be present will interfere only slightly. The sensitivity limit is 0·05 μg/cm^2 for $A = 0{\cdot}01$.

The extraction of titanium is strongly influenced by the presence of various anions (see Fig. 3).

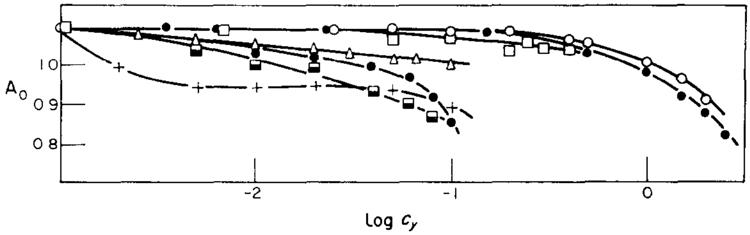

FIG. 3.—Influence of some competing ligands on the system Ti(IV)–catechol–BTPP. $c_M = 1{\cdot}10 \times 10^{-4}M$; $c_R = 0{\cdot}4M$; $c_B = 0{\cdot}005M$; $\lambda = 410$ mμ. ●—formate buffer pH 3·8; ○—glycine buffer pH 2·3; ⊙—oxalic acid; ⊕—EDTA disodium salt, tartaric acid; ⊡—citric acid; □—KCl, KNO_3; △—$NaClO_4$.

The high distribution constants for these titanium association complexes ($K_d \sim 10^4$) permit quantitative extraction of even 0·01–0·1 ppm of titanium if the volume ratio V_{org}/V_w is 0·02.

From 3 to 60 μg of titanium can be extracted from 10–500 ml of aqueous solution containing 0·5*M* catechol, 0·005*M* BTPP, 1% hydrazine sulphate and 0·1*M* formate buffer (pH 3·5), by shaking for 20 min with chloroform presaturated with water. The absorbance of the chloroform layer is measured at 410 mμ. Tungsten(VI), niobium(V) and molybdenum(VI) interfere but can be previously extracted from 3*N* sulphuric acid containing 0·4*M* catechol and 0·005*M* BTPP.

Determination of titanium(IV) in the presence of iron(III) or uranium(VI). To the acid aqueous solution containing 3–60 μg of titanium and not more than 11·2 mg of iron(III) add 2·5 ml of 5% ascorbic acid, adjust to pH 1·8, add 2 ml of 2*M* catechol and 1 ml of 0·05*M* BTPP solutions both adjusted to pH 1·8, dilute to 10 ml and extract vigorously for 10 min with 10 ml of chloroform. Measure the absorbance at 410 mμ. More than 0·5*M* chloride interferes. The determination of 3–60 μg of titanium can also be done in the presence of 11·9 mg of uranium but ascorbic acid then cannot be used.

TABLE II.—DETERMINATION OF TITANIUM(IV)

Titanium(IV)				Other ion present,
Taken, *ppm*	Found, *ppm*	$t.s/\sqrt{n}$, *ppm*	*n*	*ppm*
0·96	0·95	±0·04	4	—
4·79	4·72	±0·04	10	—
4·79	4·79	±0·06	4	Fe(III) 2·7
4·79	4·68	±0·04	4	Fe(III) 5·5
4·79	4·59	±0·06	4	Fe(III) 11·2
0·192*	0·196	±0·02	4	—
0·575*	0·563	±0·015	4	—
0·118†	0·120	±0·003	5	—

* $v_0/v_w = 0{\cdot}1$.
† $v_0/v_w = 0{\cdot}04$.

Determination of titanium in the presence of molybdenum. To the aqueous acid sample solution containing 3–60 μg of titanium and 8–250 μg of molybdenum(VI) add 2 ml of 2*M* catechol solution, adjust to pH 1·6–2 and add 15 ml of 0·05*M* BTPP. Dilute to 10 ml and extract for 10 min with 10 ml of chloroform. Measure the absorbance of the chloroform layer at 410 and 660 mμ and evaluate the results in the usual way for two-component analysis. The absorbance at 680 mμ corresponds to the molybdenum species only.

TABLE III.—SIMULTANEOUS DETERMINATION OF TITANIUM(IV) AND ONE OF MOLYBDENUM(VI), TUNGSTEN(VI) AND NIOBIUM(V)

Taken, *ppm*			Found, *ppm*					
Ti(IV)	Other ion		Ti(IV)	$t.s/\sqrt{n}$	Other ion		$t.s/\sqrt{n}$	*n*
1·93	Mo(VI)	3·84	1·90	±0·0	Mo(VI)	3·90	±0·11	4
0·48		17·28	0·47	±0·03		17·22	±0·22	5
0·48	W(VI)	29·40	0·49	±0·01	W(VI)	29·94	±0·42	4
1·44		14·70	1·47	±0·02		15·41	±0·61	4
0·96	Nb(V)	2·79	0·98	±0·02	Nb(V)	2·83	±0·14	4

Niobium(V)

Various yellow species are extracted into chloroform from aqueous 0·4*M* catechol solutions in the presence of BTPP over a large acidity range up to 12*N* sulphuric acid. The absorbance of the organic layer is constant over the acidity range from 7*N* sulphuric acid to pH 2·4, and again at pH >3·0; λ_{max} occurs at 344 mμ for extraction from 2*N* sulphuric acid and 317 mμ for extraction at pH 6. At pH 0–2·5 the extraction of niobium is but little influenced by the presence of 0·01*M* oxalic acid, 0·01*M* citric acid and 0·02*M* tartaric acid, and 0·05*M* tartaric acid or 0·01*M* fluoride do not interfere at pH 4·7.

However, the degree of extraction is considerably influenced by the sequence of mixing the components in the aqueous layer. Niobium as niobate solution saturated with potassium carbonate must always be added to the aqueous solution containing all the other reacting components. The absorbance of the chloroform layer is 25% lower if the initial niobium solution contains 0·05*M* oxalic or tartaric acid. With solutions containing less than 0·4*M* catechol the extraction curves are considerably shifted towards lower acidities and results are inconsistent.

The spectrophotometric determination is only possible if the niobium is extracted from aqueous solutions containing 0·4*M* catechol, 0·01*M* BTPP and 2–5*N* sulphuric acid (see Table IV).

The Lambert-Beer law is obeyed at 345 or 410 mμ for 1·5–9·5 ppm of niobium extracted into chloroform; $\varepsilon = (6{\cdot}44 \pm 0{\cdot}09) \times 10^4$ at 345 mμ and $(1{\cdot}73 \pm 0{\cdot}02) \times 10^4$ at 410 mμ, and the sensitivity at 410 mμ is 0·16 $\mu g/cm^2$ for $A = 0{\cdot}01$. Tungsten interferes under the conditions given, but titanium(IV), vanadium(IV), iron(III) and uranium(VI) do not. Two-component analysis of the absorbance at 660 and 410 mμ can be used for the simultaneous determination of molybdenum and niobium.

Tungsten(VI)

Tungsten(VI) is extracted into chloroform, dichloromethane or 1,2-dichloroethane over a large acidity range from solutions containing catechol and BTPP in excess, giving bright orange solutions with λ_{max} at 335 and 445 mμ. The absorbance of the organic layer is constant if extraction is made from solutions containing 0·1–0·4*M* catechol and 0·005*M* BTPP at acidities from pH 2·2 to 15*N* sulphuric acid (Fig. 4). However, the extraction is far from quantitative with less than 0·1*M* catechol, and the results depend on the order of mixing the components and the manner of adjusting the pH in the aqueous layer if chloroform is used as extractant. Dichloromethane and 1,2-dichloroethane give more reproducible results.

Beer's law is obeyed for 1·8–36·0 ppm of tungsten for all the solvents mentioned if extraction is made from 0·4*M* catechol, 0·005 BTPP and 2–3·5*N* sulphuric acid media, $\varepsilon = (6{\cdot}44 \pm 0{\cdot}07) \times 10^3$ at 440 mμ, the sensitivity being 0·29 μg/cm² for $A = 0{\cdot}01$. Vanadium(IV) and iron(III) do not interfere if tungsten is extracted from 3–10*N* sulphuric acid. In the presence of molybdenum the absorbances at 440 and 660 mμ are evaluated by the two-component procedure. Titanium up to 1·9 ppm does not interfere but niobium interferes strongly (see Table IV).

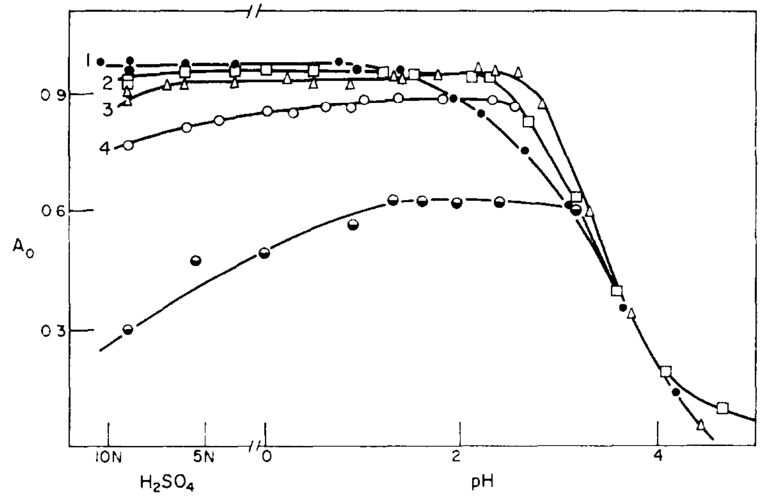

FIG. 4.—pH-Absorbance curves for the system W(VI)–catechol–BTPP.
$c_M = 1{\cdot}5 \times 10^{-4}M$; $c_B = 0{\cdot}005M$; $\lambda = 440$ mμ.
c_R: *1*—0·4*M*; *2*—0·2*M*; *3*—0·1*M*; *4*—0·05*M*; *5*—0·02*M*.

Molybdenum(VI)

Aqueous solutions of molybdate containing an excess of catechol are yellow or yellowish orange and become deep orange on addition of BTPP, but a blue-green species (λ_{max} 420 and 650 mμ) is extracted into chloroform over an acidity range from 9*N* sulphuric acid to pH 2·4. Extraction is maximal for the acidity range from 3*N* sulphuric acid to pH 1·0 and is considerably influenced by the catechol concentration if this is less than 0·4*M*. A partially-reduced molybdenum(VI)–molybdenum(V)–catechol–BTPP species is extracted under these conditions. The yellow molybdenum(VI)–catechol–BTPP complex is only extracted at pH >3·4 (λ_{max} 390 mμ) (Fig. 5). The Lambert-Beer law is obeyed for 1·5–20 ppm of molybdenum; $\varepsilon = (6{\cdot}45 \pm 0{\cdot}31) \times 10^3$ at 650 mμ, $(6{\cdot}78 \pm 0{\cdot}04) \times 10^3$ at 410 mμ and $(5{\cdot}55 \pm 0{\cdot}10) \times 10^3$ at 730 mμ, in chloroform. The sensitivity at 650 mμ is 0·14 μg/cm² for $A = 0{\cdot}01$.

For its spectrophotometric determination, molybdenum should be extracted into chloroform from 0·4*M* catechol and 0·001*M* BTPP medium at an acidity between 3·6*N* (sulphuric acid) and pH 1·5. The determination becomes selective if the absorbance of the organic layer is measured at 650 mμ since the analogous titanium(IV), niobium(V), tungsten(VI), iron(III) and uranium(VI) complexes either do not absorb at this wavelength or are not extracted under these conditions of acidity.

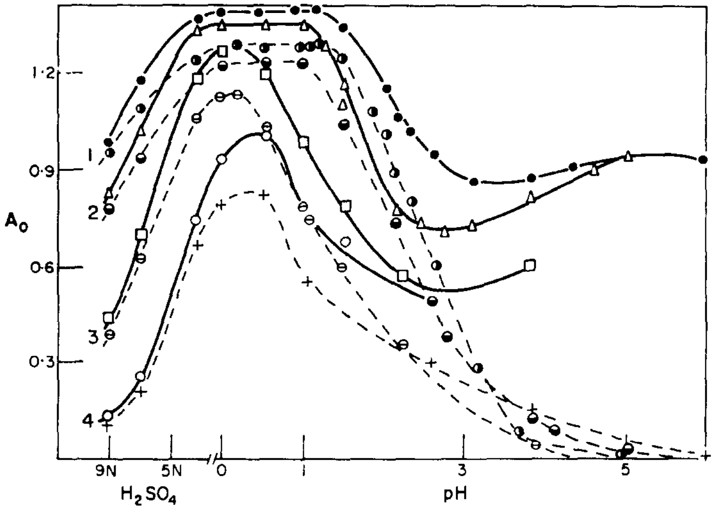

FIG. 5.—pH-Absorbance curves for the system Mo(VI)–catechol–BTPP.
$c_M = 2·0 \times 10^{-4}M$; $c_B = 0·05M$.
c_R: *1*—0·4*M*; *2*—0·2*M*; *3*—0·1*M*; *4*—0·05*M*.
———420 mμ; – – – –650 mμ.

Simultaneous determination of titanium(IV) and niobium(V) or tungsten(VI) and titanium(IV)

To the acid aqueous sample solution (not more than 5 ml) containing 3–60 μg of titanium and 16–400 μg of tungsten or 2–60 μg of niobium, add 2 ml of 2*M* catechol solution, 2 ml of sulphuric acid (1 + 1) and 1 ml of 0·05*M* BTPP, dilute to 10 ml, and extract for 15 min with 10 ml of chloroform. Only tungsten and niobium are extracted under these conditions and the absorbance at 440 mμ gives the tungsten content, and that at 410 or 340 mμ gives niobium. To a 5-ml aliquot of the aqueous layer after the first extraction add 2 ml of 2*M* catechol, 1 ml of 0·05*M* BTPP and 1 ml of 1*M* formate buffer solution (pH 3·6) containing 5% of hydrazine hydrate, adjust to pH 1·6–3·0, dilute to 10 ml and extract with chloroform as before. The concentration of titanium is evaluated from the absorbance at 410 mμ (Table III).

TABLE IV.—DETERMINATION OF TUNGSTEN(VI), MOLYBDENUM(VI) AND NIOBIUM(V)

Taken, *ppm*		Found, *ppm*		$t.s/\sqrt{n}$, *ppm*		*n*
W(VI) 7·35		W(VI) 7·15		±0·19		7
29·40		29·41		±0·69		7
Mo(VI) 3·84		Mo(VI) 3·86		±0·12		7
19·10		19·08		±0·20		7
Nb(V) 9·36		Nb(V) 9·34		±0·09		7
Mo(VI) 3·84	W(VI) 21·96	Mo(VI) 3·84	W(VI) 21·88	±0·05 (Mo)	±0·20 (W)	4
Mo(VI) 11·52	W(VI) 14·64	Mo(VI) 11·57	W(VI) 14·61	±0·10 (Mo)	±0·11 (W)	4

Simultaneous determination of molybdenum and tungsten

Extract from 1*M* sulphuric acid containing 0·4*M* catechol and 0·005*M* BTPP. Measure the absorbance of the organic layer at 660 and 440 mμ and treat the values according to the two-component procedure (the molybdenum complex absorbs only at 660 mμ). (See Table IV.)

Iron(III) and uranium(VI)

A red iron(III) species is extracted into chloroform from solutions containing 0·4*M* catechol and 0·01*M* BTPP, the optimum pH being 4·2; (λ_{max} = 495–510 mμ; $\varepsilon = 3·8 \times 10^3$). However, catechol is easily oxidized by iron(III) to *o*-benzoquinone, which is also extracted and interferes.

Uranium(VI) gives a brown species which is extracted under the same conditions: $\lambda_{max} = 410$ mμ; $\varepsilon = 1 \cdot 92 \times 10^3$. These two extractions are of no particular analytical interest.

Zusammenfassung—Zur Extraktion von Eisen(III), Molybdän(VI), Titan(IV), Niob(V), Vanadium(IV), Uran(VI) und Wolfram(VI) als ternäre Komplexe mit Brenzcatechin und einem quartären Kation wie n-Butyltriphenylphosphonium, n-Propyltriphenylphosphonium, Tetraphenylarsonium, Cetylpyridinium, Cetyltrimethylammonium und 2,3,5-Triphenyltetrazolium in Chloroform als Extraktionsmittel werden Vorschriften angegeben. Mit Maskierungsmitteln und pH-Kontrolle können auf diese Weise einige dieser Elemente voneinander getrennt werden.

Résumé—On présente des méthodes pour l'extraction de fer(III), molybdène(VI), titane(IV), niobium(V), vanadium(IV), uranium(VI) et tungstène(VI) à l'état de complexes ternaires avec le catéchol et un cation quaternaire tel que *n*-butyltriphénylphosphonium, *n*-propyltriphénylphosphonium, tétraphénylarsonium, cétylpyridinium, cétyltriméthylammonium et 2,3,5-triphényltétrazolium, le solvant étant le chloroforme. Par l'emploi d'agents dissimulants et le contrôle du pH, quelques-uns de ces éléments peuvent être séparés l'un de l'autre par ces moyens.

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SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM WITH 2-(1-HYDROXY-4,6-DINITRO-2-PHENYLAZO)-1,8-DIHYDROXYNAPHTHALENE-3,6-DISULPHONATE (PICRAMINE CA) AS CHROMOGENIC REAGENT

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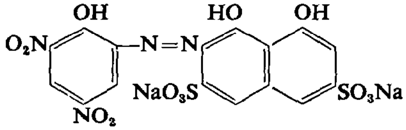
Summary—The title compound has been used as a selective reagent for the micro-determination of zirconium in acidic medium (0·5*M* HCl) and found to be better than Picramine R. Spectrophotometric studies show the formation of a 2:1 (ligand:Zr) water-soluble complex and the reaction is suitable for photometric determination of 0·4–2·8 ppm of zirconium. The colour takes about 90 min to develop fully and is stable for about 20 hr. The molar absorptivity of the complex is $2 \cdot 4 \times 10^4$ and the equilibrium constant is of the order of 10^{10}. The interference due to a number of ions has been studied.

It is only in recent years that analytical applications of azo dyes derived from picramic acid have been described. Gusev *et al.*[1] reported the use of the α-naphthol derivative in the determination of magnesium. Poluektov and Kiseleva[2] described Picramine R as a suitable reagent for indium, and Korenman *et al.*[3] studied the use of the H-acid derivative as a reagent for gallium and indium. Savvin *et al.*[4,5] reported Picramine R as a reagent for zirconium. Shchurova *et al.*[6] described the use of picramine azo derivatives of 8-hydroxyquinoline-5-sulphonic acid and H-acid as suitable metal-ion indicators for the complexometric determination of bismuth.

Very recently, Savvin *et al.*[4] have reviewed several reagents for the photometric determination of zirconium. In addition to Arsenazo III, they have suggested two new reagents, Picramine R and Nitrosulphophenol S. These dyes have been shown to be superior to Arsenazo III, as they can be used even in the presence of Th(IV), Ti(IV), La(III), rare earths and U(VI). Stilbazogall I and Stilbazogall II[7,8] have also been proposed as selective reagents for zirconium.

In the present investigations, the picramine azo derivatives of α-naphthol, β-naphthol, resorcinol, 1-hydroxy-2-naphthoic acid, 2-hydroxy-3-naphthoic acid, H-acid, 1-naphthol-5-sulphonic acid and chromotropic acid have been prepared. The chromotropic acid derivative, 2-(1-hydroxy-4,6-dinitro-2-phenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonate (Picramine CA), has been found suitable for the photometric determination of zirconium. It can be used in the presence of Th(IV), Ti(IV), La(III), rare earths, U(VI) and a number of other ions and is more sensitive (molar



Picramine CA

absorptivity, 2·4 × 10^4) than Picramine R (1·7 × 10^4). This dye does not seem to have been prepared earlier nor studied as an analytical reagent.

EXPERIMENTAL

Reagents

Preparation of the dye. Picramic acid (5 g) was dissolved in hot alcohol (150 ml); hydrochloric acid (1 + 1; 30 ml) was added and the mixture cooled in an ice-bath. The calculated amount of 10% sodium nitrite solution was then added slowly with constant stirring. After 15–30 min the crystalline diazo compound had precipitated. It was separated by filtration and washed with a small amount of cold water. It was then suspended in cold water (30 ml) and coupled with chromotropic acid (9 g) dissolved in water (50 ml) containing sodium carbonate (5 g). The deep violet dye was filtered off and washed with a small amount of cold water. The crude dye was purified by repeated crystallization from 50% alcohol. The acid form of the dye was finally extracted from acidic solution into n-butanol and the extract was washed with water to remove any acid present. It was further treated with alcoholic sodium hydroxide solution to obtain the insoluble disodium salt of the dye. This was filtered off and washed thoroughly with alcohol and ether and dried at 90°. The purity of the dye was confirmed by chromatography and elemental analysis.

Dye solution, 0·005*M*. Prepared in doubly distilled water, and further diluted for use.

Zirconium(IV) solution, 0·01*M*. Prepared by dissolving the requisite amount of $ZrOCl_2.8H_2O$ in 1*M* hydrochloric acid and then standardized.[9] A fresh solution was used to avoid any aging effect, and further diluted for use.

Calibration curve

In 25-ml standard flasks, place aliquots of solution containing 10–70 μg of zirconium, and 10 ml of $5 \times 10^{-4}M$ dye solution, followed by 2·5 ml of 5*M* hydrochloric acid. Dilute the contents of the flasks with doubly distilled water and set them aside for 2 hr. Measure the absorbance of the solutions against a similarily prepared reagent blank at 570 mμ.

RESULTS AND DISCUSSION

Qualitative study of the reactions of the dye revealed that it reacts with copper(II), scandium(III), zirconium(IV) and niobium(V) ions in acidic medium (~0·5*N* hydrochloric acid) to give a colour change from pink red to violet. In alkaline medium it gives a blue colour with copper(II), uranium(VI), vanadium(IV) and zirconium(IV) and a deep violet colour with a number of other ions. The colour reactions in neutral and alkaline media are not very selective, but a study of the zirconium complex of the dye in acidic medium was considered worthwhile.

Properties of the dye

Picramine CA is a deep violet powder soluble in water, stable in the solid state and in solution. An acidic solution of it ($pH < 1·5$) is pink-red (λ_{max} 500–510 mμ), whereas neutral and alkaline solutions are violet (λ_{max} 560–570 mμ). Its solution in concentrated sulphuric acid is bluish violet (λ_{max} 590 mμ).

Zirconium complex

The absorption spectra of 0·5*M* hydrochloric acid solutions containing different metal–dye ratios, measured against a dye blank, are shown in Fig. 1.

The optimum acidity was determined by plotting the absorbance of the complex as a function of the hydrochloric acid concentration and was found to be 0·5*M* (Fig. 2). As the dye absorbance is itself sensitive to changes in acid concentration in this region, it is necessary to have the same acidity in the test and blank solutions.

The absorbances of solutions containing 1:2 and 2:1 Zr(IV):dye ratios in 0·5*M*

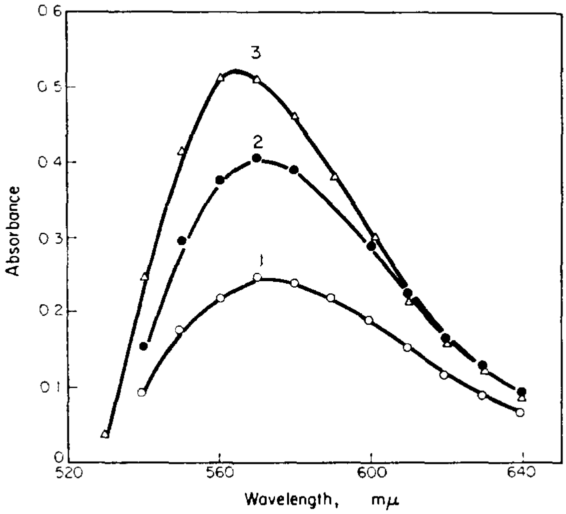


FIG. 1.—Absorption spectrum of zirconium complex.
[Zr]: [dye]; *1*—1:2; *2*—1:1; *3*—2:1. Final dye concentration 4 × $10^{-5}M$.

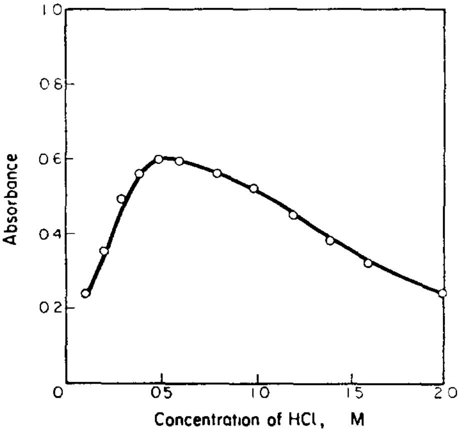


FIG. 2.—Effect of HCl concentration.
[Dye] = [Zr] = 5 × $10^{-5}M$.

hydrochloric acid were measured against dye blanks at intervals of time. The absorbance increased gradually with time, becoming constant after about an hour and a half and remaining so for about 20 hr (Fig. 3). Measurements could be made after 30 min reaction, however, if a strict time schedule were kept.

The colour system obeys Beer's law over the range 0·4–2·8 ppm zirconium. The optimum concentration range (Ringbom[10]) is 0·7–3·0 ppm. By means of Ayres' equation[11] the relative error per 1 % absolute photometric error was calculated as 2·93 %. The standard deviation was found to be 1·8 %. The molar absorptivity of the complex is 2·4 × 10^4, giving a Sandell sensitivity coefficient of 0·0038 $\mu g/cm^2$ for 0·001 absorbance.

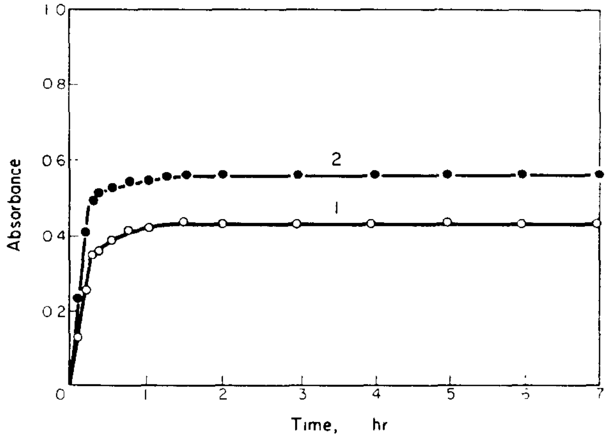


FIG. 3.—Development of colour.
[Zr]: [dye]; *1*—1:2; *2*—2:1. Final dye concentration 4 × $10^{-5}M$.

Effect of foreign ions

In the determination of 2·0 ppm of zirconium, Li, Na, K, Mg, Ca, Sr, Ba do not interfere when present up to 50 ppm; Cd(II), Hg(II), Zn(II), Pb(II), Ni(II), Co(II), Cr(III), Ga(III), In(III), Tl(III), As(III), Sb(III) and Bi(III) do not interfere when present up to 10 ppm; Mn(II), Fe(II), Pd(II), La(III), Y(III), rare earths, Ti(IV), Th(IV), V(IV), Pt(IV), U(VI), Mo(VI) and W(VI) do not interfere when present up to 5 ppm. The effect of 5 ppm of V(V) and Fe(III) can be overcome by adding hydroxylamine hydrochloride. However, Cu(II), Nb(V), EDTA, fluoride, sulphate, tartrate, citrate, and other ions which form complexes with zirconium(IV), interfere.

The standard spectrophotometric methods[12–15] indicated that a 1:2 (metal:dye) complex was formed but not others. For complete reaction the [dye]: [Zr] ratio must be at least 4 (Fig. 4). The conditional formation constant (in 0·5M hydrochloric acid at 30°) and free energy of formation have been calculated by the molar ratio[15] and Job methods[13]. The values are log K = 10·60, $\Delta G^\circ = -14{\cdot}7$ kcal/mole.

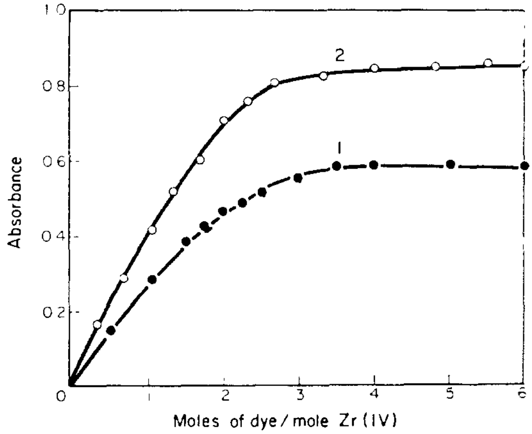


FIG. 4.—Mole-ratio method.
[Zr]; *1*—2 × $10^{-5}M$; *2*—3 × $10^{-5}M$.

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Zusammenfassung—Die im Titel genannte Verbindung wurde als selektives Reagens zur Mikrobestimmung von Zirkonium in saurem Medium (0,5*M* HCl) verwendet und für besser als Pikramin R befunden. Spektrophotometrische Untersuchungen zeigen die Bildung eines wasserlöslichen 2:1-(Ligand:Zr) Komplexes an; die Reaktion eignet sich dauert etwa 90 min, bis die Farbe voll entwickelt ist; dann ist sie etwa 20 h stabil. Der molare Extinktionskoeffizient des Komplexes beträgt $2{,}4 . 10^4$, die Gleichgewichtskonstante liegt in der Größenordnung von 10^{10}. Die Störung durch eine Anzahl von Ionen wurde untersucht.

Résumé—On a utilisé le composé du titre comme réactif sélectif pour le microdosage du zirconium en milieu acide (HCl 0,5*M*) et l'a trouvé meilleur que la Picramine R. Les études spectrophotométriques montrent la formation d'un complexe hydrosoluble 2:1 (ligand: Zr) et la réaction convient au dosage photométrique de 0,4–2,8 p.p.m. de zirconium. Il faut environ 90 mn pour le développement complet de la coloration, qui est stable pendant environ 20 h. Le coefficient d'absorption moléculaire du complexe est de $2{,}4 \times 10^4$ et la constante d'équilibre est de l'ordre de 10^{10}. On a étudié les interférences dues à un certain nombre d'ions.

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EIN NEUES REAGENZ ZUR FLUOROMETRISCHEN BESTIMMUNG VON TERBIUM(III) UND DYSPROSIUM(III) IN WÄSSRIGER LÖSUNG

BIS[1(2)-PYRIDYL-3-METHYL-5-PYRAZOLONYL]-4,4'-METHAN

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Zusammenfassung—Bis[1(2)-pyridyl-3-methyl-5-pyrazolonyl]-4,4'-methan wurde aus 1(2)-pyridyl-3-methyl-5-pyrazolon und Urotropin synthetisiert. Die Struktur wurde mit Hilfe von Molekulargewichtsbestimmungen, UV-, IR-, and NMR-Spektren aufgeklärt. Die Fluoreszenzspektren der wässrigen Lösung der Tb-, Dy- and Sm-Komplexe sowie die Abhängigkeit der relativen Fluoreszenzintensität vom pH-Wert, vom Verhältnis Metall: Komplexbildner und von den anderen Seltenen-Erd-Ionen werden mitgeteilt. Die analytische Bestimmung der Elemente Dy(III) und Tb(III) in den Seltenen-Erden wird beschrieben.

In letzter Zeit wurden zur fluorometrischen Bestimmung der Elemente Terbium und Dysprosium Pyrazolonderivate mit gutem Erfolg angewandt.[1-3] Von den eingesetzten Verbindungen ergab aber nur das 1-Sulphophenylmethyl-3-pyrazolon-5 Komplexe mit Terbium und Dysprosium, die in wässriger Lösung fluoreszierten. Die Komplexe der anderen Derivate sind nur im festen Zustand beständig.

Bei unseren Untersuchungen zur Bestimmung der Seltenen Erden auf der Grundlage der Fluoreszenzanalyse konnten wir das neue Reagenz Bis(1(2)-pyridyl-3-methyl-5-pyrazolonyl)-4,4'-methan (BPPM) synthetisieren, das mit Terbium und Dysprosium in wässriger Lösung Komplexe bildet, die rund zehnmal intensiver fluoreszieren als die Komplexe der obengenannten Verbindung. Damit ist die Bestimmung von Terbium in der Größenordnung von 10^{-2} bis $10^{-3}\%$ und des Dysprosiums in der Größenordnung von 10^{-1} bis $10^{-2}\%$ in den Seltenen Erden möglich.

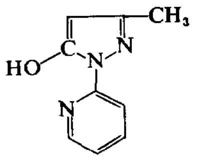
Synthese

1(2)-Pyridyl-3-methyl-5-pyrazolon (PP) (200 mg), das nach Fargher[4] hergestellt worden war, wurde in Wasser (100 ml) mit leichtem Erwärmen gelöst. Nach dem Erkalten der klaren Lösung wurde dann festes Urotropin (660 mg) hinzugefügt. Nach einiger Zeit fiel eine farblose, stark verfilzte Kristallmasse aus. Der Niederschlag wurde abgesaugt, mit Wasser gewaschen und im Exikator über $CaCl_2$ getrocknet. Ausbeute 60–70%, bezogen auf PP. Fp. 213° unter Zersetzung. Fp. von PP: 110°. BPPM löst sich sowohl im sauren als auch alkalischen Milieu.

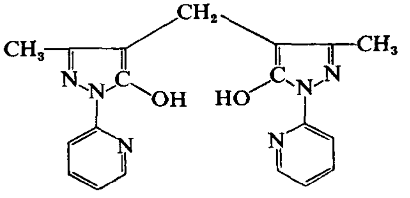
Strukturuntersuchungen

Die ebullioskopische Molmasse-Bestimmung in $CHCl_3$ ergab einen mittleren Wert von 366. Dieser Wert entspricht etwa der doppelten Molmasse (350) des eingesetzten PP. Es liegt nahe, eine Kondensation zwischen zwei Moleküle des PP

(Formel I) mit Formaldehyd anzunehmen. Der entstandenen Verbindung käme dann Formel II zu.



I



II

Die Werte der Mikroanalyse (gef.: C = 62,1 %; H = 4,9 %; N = 22,9 %, ber.: C = 62,9 %; H = 4,9 %; N = 23,2 %) stimmen gut mit den berechneten Werten der angenommenen Verbindung überein, liefern aber keinen Beweis für die obige Formel, da die Werte der prozentualen Zusammensetzung der Ausgangssubstanz innerhalb der Fehlergrenzen der Mikroanalyse den gleichen Betrag haben. Aber der um 100° höhere Schmelzpunkt und die ermittelte Molmasse legen diese Formulierung nahe.

Auch das Verhalten der beiden Komplexbildner gegenüber Cu(II) ist verschieden. Nur das BPPM bildet mit Kupfer einen in Alkohol fast unlöslichen rotvioletten 1:1-Komplex.

Analyse: gef.: Cu = 14,4 %; C = 52,3 %; H = 3,6 %; N = 19,2 %.
ber.: Cu = 14,85 %; C = 53,81 %; H = 3,74 %; N = 19,74 %.

Die Zweiwertigkeit des Cu in dieser Verbindung wird durch das magnetische Moment von 1,72 BM bestätigt.

Durch spektroskopische Untersuchungen werden weitere Beweise für die obige Formulierung geliefert.

UV-Spektren. Die Kondensation zweier Moleküle PP mit Formaldehyd führt zu keiner merklichen Änderung der Elektronenverteilung in den Molekülen. Die UV-Spektren des PP und BPPM müßten praktisch identisch sein bis auf die molaren Extinktionskoeffizienten, die von BPPM etwa doppelt so groß sein sollten. Die in Tabelle I wiedergegebenen Ergebnisse stimmen damit gut überein.

TABELLE I.—UV-SPEKTREN 10^{-5} MOLARER METHANOLISCHER LÖSUNGEN VON PP UND BPPM

Verbindung	λ_{max}, *nm*	ε_{max}
PP	227	$5 \cdot 10^3$
	252	$1{,}5 \cdot 10^4$
	292	$8{,}5 \cdot 10^3$
BPPM	227	$9{,}8 \cdot 10^3$
	253	$1{,}7 \cdot 10^4$
	296	$1{,}2 \cdot 10^4$

TABELLE II.—NMR-SPEKTREN VON PP UND BPPM IN $CDCl_3$ MIT TMS ALS STANDARD

Verbindung	chemische Verschiebung *ppm*
PP	2,25 CH_3 1
	3,47 CH_2 2
	5,40 CH 3
BPPM	2,27 CH_3 1
	3,40 CH_2 2

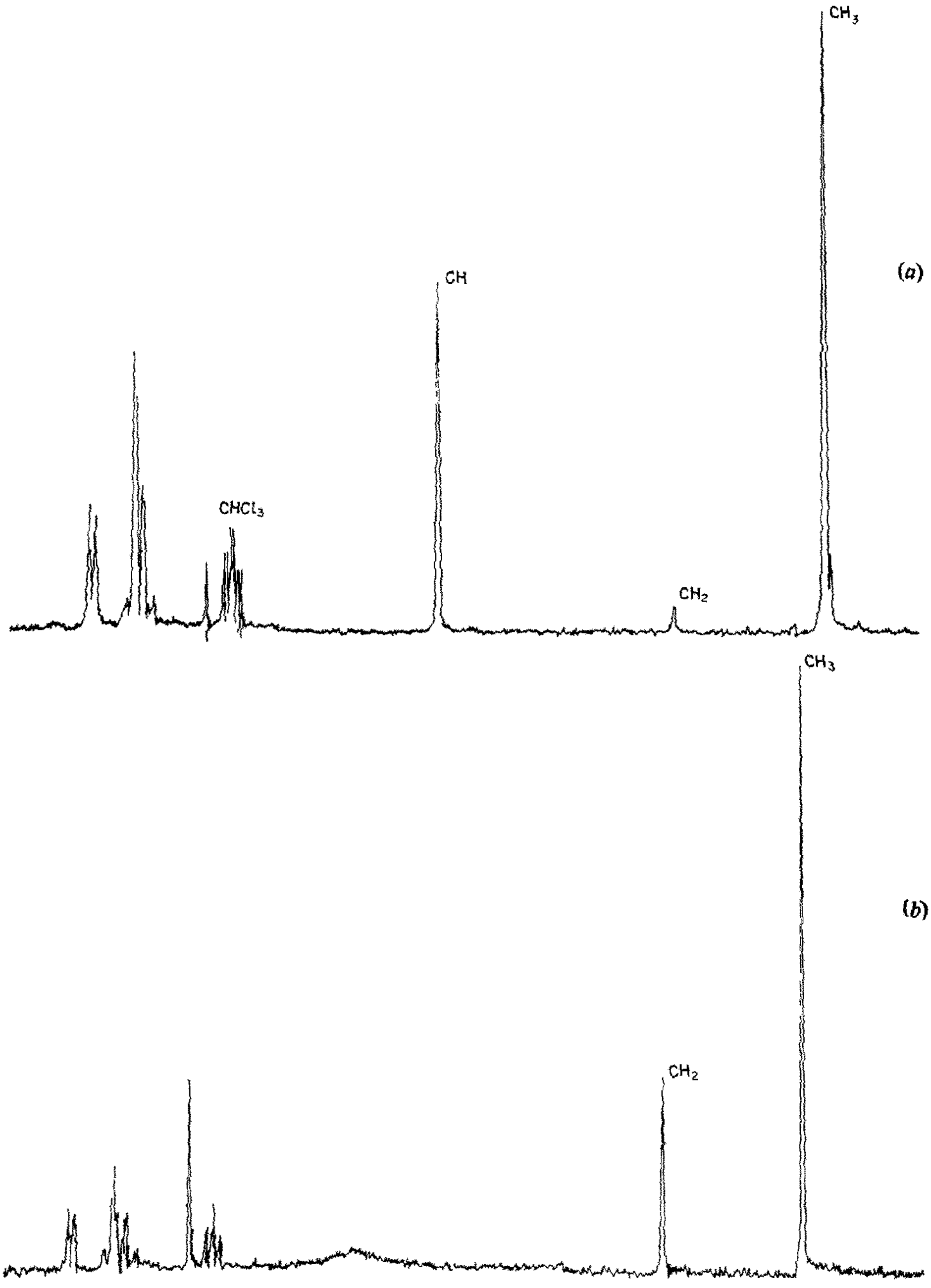


Abb. 1.—NMR-Spektren von PP (*a*) und BPPM (*b*) in $CDCl_3$.

IR-Spektren. Die Chloroformlösungen der untersuchten Verbindungen ergaben praktisch identische Spektren. Nur die Intensitäten der C=O-Frequenz bei 1730 cm^{-1} unterscheiden sich merklich. Im PP ist die Intensität größer, aber immer noch geringer als in anderen C=O-Verbindungen. Dies weist auf das Vorliegen eines tautomeren Gleichgewichts hin. Die C=O-Frequenz im BPPM ist nur sehr schwach ausgeprägt, ein Zeichen dafür, daß diese Verbindung fast ausschließlich in der Enolform vorliegt.

NMR-Spektren (Tabelle II, Abb. 1). Entsprechend dem Keto-Enolgleichgewicht sollten für das PP außer den Pyridinprotonsignalen folgende Signale zu beobachten sein: CH_3, CH_2, CH und OH und für das BPPM, das fast ausschließlich in der Enolform vorliegt, CH_3, CH_2 und OH.

Im Spektrum des PP werden CH_3^-, CH_2^- und CH-Signale beobachtet, wobei die Intensität des CH-Signals wesentlich stärker ist als die des CH_2-Signals. Folglich muß das Keto-Enolgleichgewicht zum großen Teil auf der Seite der Enolform liegen. Im Spektrum des BPPM ist kein CH-Signal zu beobachten, wohl aber ein intensives CH_2-Signal. Dieser Befund ist ein ausreichender Beweis für die in Formel II beschriebene Struktur der neu synthetisierten Verbindung.

Fluoreszenzeigenschaften der untersuchten wässrigen Lösung

Die Intensität der charakteristischen Linienfluoreszenz der dreiwertigen Elemente Samarium, Europium, Terbium und Dysprosium kann durch Komplexbildung erhöht werden, wenn der Ligand im UV-Bereich absorbiert und wenn sein Triplettzustand höherliegt als das Resonanzniveau des betreffenden SE-Ions.[5] Bei Bestrahlungen mit UV-Licht erfolgt die Anregung der SE-Ionen nicht über die relativ schmalen und wenig intensiven SE-UV-Absorptionsbanden, sondern über die viel breiteren und intensiveren Ligandenabsorptionsbanden. Die Energie wird dann strahlungslos an das SE-Ion übertragen und als charakteristische Fluoreszenzstrahlung emittiert, die zum Nachweis und zur Bestimmung dieser Elemente verwendet werden kann. Die Effektivität der strahlungslosen Energieübertragung ist vom Liganden und dem Medium stark abhängig.

Das neu synthetisierte Reagenz BPPM überträgt die Anregungsenergie wirkungsvoll auf das Terbium und Dysprosium, schwächer auf das Samarium, aber unverständlicherweise auf das Europium nicht.

Die Fluoreszenzspektren wurden von $1{,}4 \cdot 10^{-4}$ molaren wässrigen Tb-, Dy- und Sm-Lösungen aufgenommen. Das Verhältnis Metall zu Ligand betrug 1:2 bei einem pH-Wert von 7,5. Zur Aufnahme der Spektren wurde das UV-Vis-Einstrahlphotometer mit Fluoreszenzaufsatz von VEB Carl Zeiss Jena verwendet. Zur Verbesserung des Signal-Rausch-verhältnisses wurde der durch das modulierte Fluoreszenzlicht erzeugte Photostrom schmalbandig verstärkt und phasenempfindlich gleichgerichtet. Die Anregung erfolgte mit einer Hg-Höchstdampfdrucklampe HBO 200 über ein Schottfilter UG 5 (Abb. 2).

Die Spektren (Tab. III, IV, V und Abb. 3) zeigen die typische Linienfluoreszenz dieser dreiwertigen Ionen. Aus den Tabellen ist zu sehen, daß die intensivste Linie des Tb bei 549,5 nm, die des Dy bei 574,8 nm und die des Sm bei 648,1 nm liegt. Diese Linien wurden ausschließlich für die quantitativen Untersuchungen benutzt. Eine Bestimmung geringer Mengen von Dy in Tb und Sm ist nicht möglich, weil sich bei größeren Spaltbreiten der Übergang $^4F_{9/2}$ — $^6H_{13/2}$ des Dy mit $^5D_4$ — $^7F_4$ des Tb und $^4F_{5/2}$ — $^6H_{5/2}$ des Sm überlagert. Außerdem wird das Dy durch das Tb desaktiviert.

Im folgenden werden die Parameter, die die Fluoreszenzintensität beeinflussen, näher untersucht.

Einfluß des pH-Wertes. Von einer Tb-Lösung ($1{,}3 \cdot 10^{-4}$ mol) mit einem Metall-BPPM-Verhältnis 1:2 wurden mehrere Proben mit pH-Werten von 5,5 bis 10

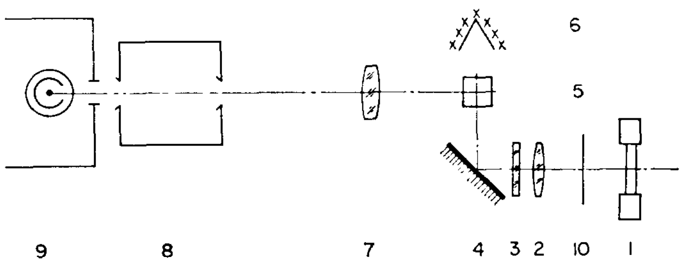


Abb. 2.—Schematischer Strahlengang des UV-Vis-Einstrahl-photometers mit Fluoreszenzaufsatz.
1—Strahler (HBO 200). 2—Quarzlinse. 3—Filter UG 5. 4—45°-Spiegel. 5—Probenküvette. 6—Absorption der Streustrahlung. 7—Quarzlinse. 8—Spiegelmonochromator SPM 2. 9—Meßeinrichtung (SEV. Verstärker, Kompensations-bandschreiber). 10—(modulator).

hergestellt. Die Einstellung des pH-Wertes erfolgte mittels Salzsäure und Ammoniak. Das Maximum der Fluoreszenzintensität ist zwischen pH-Wert 7 und 8 zu beobachten (Abb. 4).

Einfluß der BPPM-Konzentration. Bei einem pH-Wert von 7,5 und einer Tb-Konzentration von $1{,}3 \cdot 10^{-4}$ mol wurden unterschiedliche Mengen BPPM zugesetzt. Die maximale Fluoreszenzintensität wurde bei einem Verhältnis Metall:BPPM von 1:2 festgestellt (Abb. 5). Ein Überschuß des Reagenzes vermindert die Intensität. Aus diesem Grund ist die Ermittlung der Zusammensetzung des Komplexes durch isomolare Variation nicht möglich.

Abhängigkeit der Fluoreszenzintensität von den anderen SE. Zu einer Lösung von Tb (0,125 μg/ml) oder Dy (0,5 μg/ml) wurden 25 μg/ml anderer SE zugesetzt bei einem pH-Wert von 7,5 und einem Gesamtmetall-Ligand Verhältnis wie 1:2. Die Ergebnisse sind in Abb. 6 wiedergegeben. Trotz der starken Verdünnung der Lösungen ist eine starke Abhängigkeit zu beobachten, wie sie von Feststoffen und

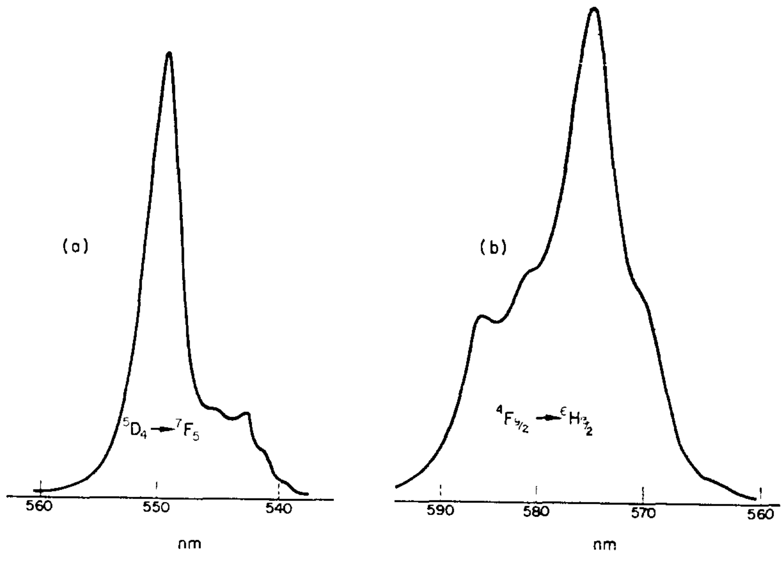


Abb. 3.—Intensivste Fluoreszenzlinien des Tb (*a*)- und Dy (*b*)-Spektrums.

TABELLE III.—FLUORESZENZSPEKTRUM DES Tb-KOMPLEXES IN WÄSSRIGER LÖSUNG

Übergang	λ, *nm*	Wellenzahl, *cm*$^{-1}$	I_{rel}
$^5D_4 - {}^7F_6$	478,3	20900	4,8
	490,8	20370	3,0
	494,9	20200	4,2
$^5D_4 - {}^7F_5$	538,6	18566	2,3
	540,8	18490	8,3
	542,4	18436	16,5
	544,0	18382	11,2
	545,0	18348	13,3
	549,3	18204	78,1
$^5D_4 - {}^7F_4$	582,1	17179	2,0
	585,2	17090	4,1
	588,9	16980	3,3
	595,3	16790	1,8
$^5D_4 - {}^7F_3$	619,0	16155	2,8
	623,0	16051	5,1
	626,0	15974	6,5
$^5D_4 - {}^7F_2$	633,0	15797	0,3
	640,8	15605	0,3
$^5D_4 - {}^7F_1$	653,7	15297	0,7
	658,3	15190	0,8
$^5D_4 - {}^7F_0$	672,6	14867	1,0

TABELLE IV.—FLUORESZENZPEKTRUM DES Dy-KOMPLEXES IN WÄSSRIGER LÖSUNG

Übergang	λ, *nm*	Wellenzahl, *cm*$^{-1}$	I_{rel}
$^4F_{9/2} - {}^6H_{15/2}$	471,3	21210	0,1
	473,0	21140	0,3
	475,6	21020	0,3
	479,3	20860	0,6
	481,9	20750	0,7
$^4F_{9/2} - {}^6H_{13/2}$	563,9	17733	0,1
	570,1	17540	1,3
	574,8	17390	3,3
	581,3	17200	1,5
	586,1	17060	1,4

TABELLE V.—FLUORESZENZPEKTRUM DES Sm-KOMPLEXES IN WÄSSRIGER LÖSUNG

Übergang	λ, *nm*	Wallenzahl, *cm*$^{-1}$	I_{rel}
$^4G_{5/2} - {}^6H_{5/2}$	561,0	17826	0,01
	564,3	17730	0,13
$^4G_{5/2} - {}^6H_{7/2}$	593,4	16852	0,1
	596,6	16761	0,07
	601,2	16633	0,13
	604,0	16556	0,11
	611,2	16363	0,27
$^4G_{5/2} - {}^6H_{9/2}$	644,0	15527	0,2
	648,1	15432	0,83
	654,5	15280	0,22
	661	15128	0,08

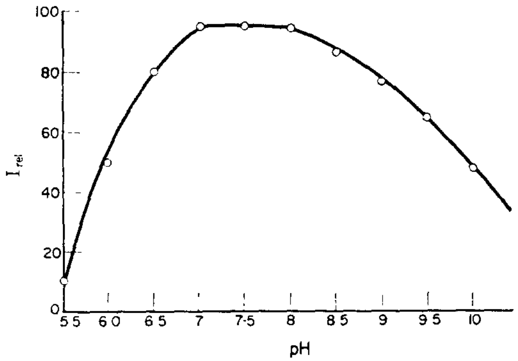


Abb. 4.—Die Abhängigkeit der Fluoreszenzintensität vom pH-Wert einer $1.3 \cdot 10^{-4}$ mol Tb-Lösung (Metall:BPPM = 1:2).

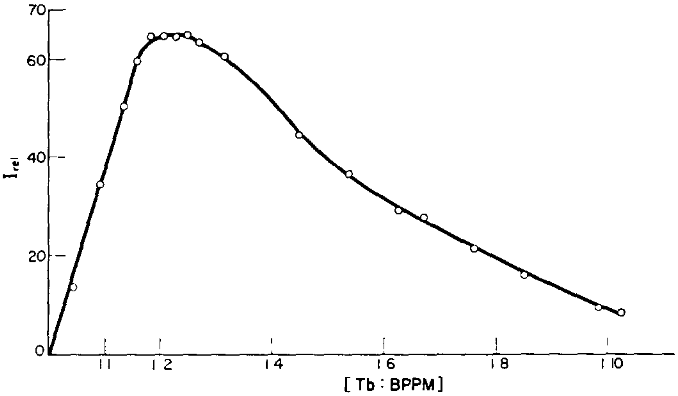


Abb. 5.—Einfluß des Verhältnisses Metall:Komplexbildner auf die Fluoreszenzintensität (pH-Wert 7,5, $c_{Tb} = 1{,}3 \cdot 10^{-4}$ mol).

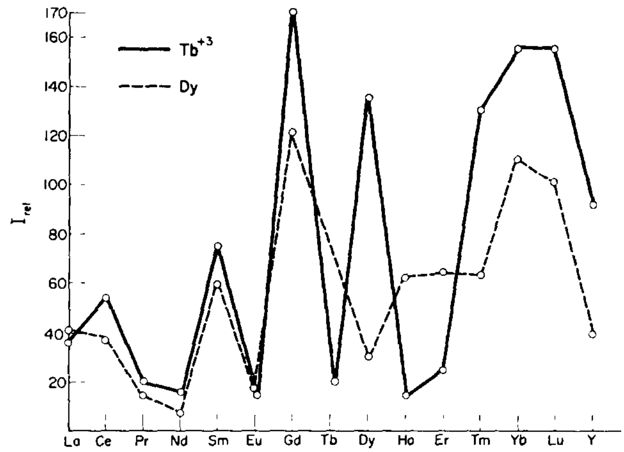


Abb. 6.—Abhängigkeit der Fluoreszenzintensität des Tb und Dy von den anderen SE Untersuchungsbedingungen: pH = 7,5, Gesamtmetall:Ligand = 1:2; $c_{Se} = 25$ μg/ml, $c_{Tb} = 0{,}125$ μg/ml, $c_{Dy} = 0{,}5$ μg/ml; bei der Tb-Messung 0,1 mm spaltbrate und Meßbereich 2, für Dy 0,5 mm spaltbrate und Meßbereich 1.

konzentrierten Lösungen wohl bekannt ist.[6] Diese Erscheinung kann damit erklärt werden, daß hier in Lösung polynukleare Komplexe vorliegen, die entsprechend dem Konzentrationsverhältnis die in der Lösung vorhandenen SE-Ionen enthalten. Durch den Zusatz eines anderen SE-Ions und der entsprechenden Menge Ligand entstehen größere polynukleare Gebilde, die eine größere Absorption aufweisen. Damit steht pro Atom Terbium oder Dysprosium mehr Anregungsenergie zur Verfügung, unter der Voraussetzung, daß innerhalb der polynuklearen Komplexe eine strahlungslose Energieübertragung stattfindet. Ist in diesem polynuklearen Komplex ein SE-Ion enthalten, das als unmittelbarer Energieüberträger (Gd) auftreten kann, dann tritt eine weitere Verstärkung auf. Elemente, die als Löscher (Nd, Pr, Ho, Er) für Terbium und Dysprosium bekannt sind, verringern die Intensität etwa um den gleichen Betrag wie sie durch die Erhöhung der Absorption durch Vergrößerung der polynuklearen Gebilde zunimmt.

Bildungsgeschwindigkeit des Komplexes

Die Bildungsgeschwindigkeit der emitierenden Verbindung bei 25° (Abb. 7, Kurve 1) ist ein weiterer Hinweis auf die Bildung polynuklearer Komplexe. Innerhalb der Bestimmungszeit bleibt die Fluoreszenzintensität konstant (Abb. 7, Kurve 2).

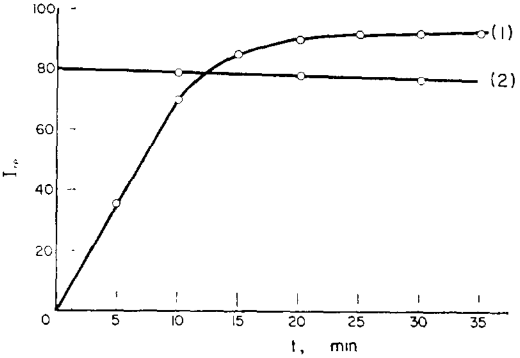


ABB. 7.—1. Bildungsgeschwindigkeit des emitierenden Komplexes. 2. Abhängigkeit der Fluoreszenzintensität von der Belichtungszeit.
c_{Tb} = 1,3.10^{-4} mol; pH-Wert = 7,5; Metall:Ligand 1:2; Temperatur = 25°C.

In Gegenwart der anderen SE-Ionen (c_{SE} = 25 μg/ml) ist die Fluoreszenzintensität im Bereich von 0,005 bis 1,5 μg/ml Terbium der Konzentration direkt proportional.

Auf Grund der starken Abhängigkeit der Fluoreszenzintensität von der Matrix wurde zur Ermittlung der Terbium- und Dysprosium-Mengen die Additionsmethode angewandt.

Herstellung der Lösungen

Die Reagenzlösung wurde aus 60 mg BPPM, die in 10 ml Wasser und 0,25 ml NH_3-Lösung (3,4 %) unter Rühren gelöst und dann auf 20 ml aufgefüllt wurden, bereitet. Der pH-Wert betrug *ca.* 10. Die Lösung mußte jeden Tag frisch hergestellt werden.

Zur Bereitung der SE-Lösungen wurden handelsübliche SE-Oxide verwendet, Lieferwerk VEB Stickstoffwerk Piesteritz. SE-Oxide (25 mg) wurden mit konzentrierter Salzsäure in das Chlorid überführt. Nachdem die überschüssige Säure durch Eindampfen beseitigt war, wurde der Rückstand in 100 ml Wasser gelöst, der pH-Wert der Lösung betrug *ca.* 5.

Durchführung der Analyse

In drei 10-ml-Kolben wurde jeweils 0,4 ml der hergestellten Reagenzlösung gegeben. Zu diesen Lösungen wurden dann je 1 ml (25 μg/ml) der auf Terbium oder Dysprosium zu untersuchenden Lösungen und zusätzlich in 2 Kolben unterschiedliche Mengen (0,025 bis 10 μg) von Terbium bzw. Dysprosium hinzugefügt und mit 2 ml Wasser verdünnt. Nach 30 Minuten wurden die Proben auf 10 ml aufgefüllt und mit dem oben beschriebenen Gerät nach Einstellung der entsprechenden Empfindlichkeit gemessen. Die unbekannten Terbium- oder Dysprosium-Mengen (x) in den SE-Oxiden wurden anhand des aufgenommenen Spektrums nach der bekannten Formel

$$x = \frac{h_x \cdot c}{h_{x+c} - h_x}$$

berechnet.

h_x = Peak-Höhe in mm der Linie der zu untersuchenden Lösung
h_{x+c} = Peak-Höhe in mm der Linie zu untersuchenden Lösung + Standardlösung
c = zugesetzte Menge an Terbium oder Dysprosium in μg

In den Tabellen VI und VII sind die erhaltenen Ergebnisse dieser Untersuchung zusammengestellt. Aus diesen Tabellen kann auch die Genauigkeit des Verfahrens abgelesen werden.

Ein Vergleich zwischen den hier mitgeteilten Nachweisverfahren und den von Kononenko[1] angegebenen ergibt, daß sie, abgesehen von einigen Ausnahmen, die gleichen Ergebnisse liefern. Jedoch wurde mit dem Reagenz 4-Sulphonyl-3-methyl-5-pyrazolon unter den hier beschriebenen optischen Aufnahmebedingungen eine

TABELLE VI.—BESTIMMUNG VON Tb_4O_7 IN SE-OXIDEN

	Tb-Gehalt des Oxids, %	zugegebene Menge, %	Gesamtmenge, %	gefundene Gesamtmenge, %	Differenz, %
La_2O_3	—	0,020	0,020	0,018	−0,002
		0,040	0,040	0,034	−0,006
CeO_2	—	0,010	0,01	0,012	+0,002
		0,040	0,04	0,037	−0,003
Pr_6O_{11}	0,011	0,010	0,021	0,0164	−0,0046
		0,020	0,031	0,032	+0,001
		0,040	0,051	0,0542	+0,0033
Nd_2O_3	—	0,01	0,01	0,014	+0,004
		0,04	0,04	0,040	0
Sm_2O_3	0,014	0,004	0,018	0,022	+0,004
		0,02	0,034	0,037	+0,003
Eu_2O_3	0,018	0,01	0,028	0,031	+0,003
		0,02	0,038	0,034	−0,004
Gd_2O_3	0,028	0,002	0,03	0,035	+0,005
		0,01	0,038	0,040	+0,002
		0,02	0,048	0,051	+0,003
Dy_2O_3	0,037	0,01	0,047	0,043	−0,004
		0,02	0,057	0,054	−0,003
		0,04	0,077	0,082	+0,005
Ho_2O_3	0,022	0,01	0,032	0,036	+0,004
		0,02	0,042	0,040	−0,002
		0,04	0,062	0,059	−0,003
Er_2O_3	0,01	0,01	0,02	0,018	−0,002
		0,02	0,03	0,03	0
Tm_2O_3	0,0184	0,002	0,0204	0,0160	−0,0044
		0,02	0,0284	0,031	+0,0026
Yb_2O_3	0,009	0,002	0,011	0,0126	+0,0016
		0,02	0,029	0,027	−0,002
Lu_2O_3	0,0146	0,002	0,0166	0,0178	+0,0012
		0,01	0,0246	0,0238	−0,0008
Y_2O_3	0,034	0,004	0,0380	0,04	+0,0018
		0,01	0,0440	0,0438	−0,0004
		0,02	0,0540	0,052	−0,0022

Tabelle VII.—Bestimmung von Dy_2O_3 in SE-Oxide

	Dy-Gehalt des Oxids, %	zugesetzte Menge, %	Gesamtmenge, %	gefundene Gesamtmenge, %	Differenz, %
La_2O_3	—	0,1	0,1	0,13	+0,03
		0,2	0,2	0,16	−0,04
		0,4	0,4	0,41	+0,01
CeO_2	—	0,1	0,1	0,11	+0,01
		0,2	0,2	0,26	+0,06
		0,4	0,4	0,37	−0,03
Pr_6O_{11}	—	0,1	0,1	0,06	−0,04
		0,2	0,2	0,18	−0,02
		0,4	0,4	0,44	+0,04
Nd_2O_3	—	0,1	0,1	0,08	−0,02
		0,2	0,2	0,19	−0,01
		0,4	0,4	0,36	−0,04
Eu_2O_3	—	0,1	0,1	0,05	−0,05
		0,2	0,2	0,23	+0,03
		0,4	0,4	0,4	0
Gd_2O_3	—	0,1	0,1	0,11	+0,01
		0,2	0,2	0,22	+0,02
Ho_2O_3	0,06	0,1	0,16	0,170	+0,01
		0,2	0,26	0,23	−0,03
Er_2O_3	—	0,2	0,2	0,165	−0,035
		0,4	0,4	0,42	0,02
Tm_2O_3	—	0,1	0,1	0,11	+0,01
		0,2	0,2	0,23	0,03
Yb_2O_3	—	0,1	0,1	0,08	−0,02
		0,2	0,2	0,2	0
Lu_2O_3	—	0,1	0,1	0,095	−0,005
		0,2	0,2	0,185	−0,015
Y_2O_3	—	0,1	0,1	0,075	−0,025
		0,2	0,2	0,193	−0,007

10mal geringere Empfindlichkeit festgestellt. Gegenüber der kürzlich mitgeteilten Bestimmung des Terbium mit EDTA-Sulphosalicylsäure[7] zeigt das BPPM mit Terbium eine 20mal höhere Intensität.

Wir danken Herrn cand. chem. G. Beuchel für die zeitweilige Mitarbeit und Herrn Dr. Klose vom Physikalischen Institut der Karl Marx-Universität Leipzig für die Anfertigung der NMR-Spektren.

Summary—The compound bis[1(2)pyridyl-3-methyl-5-pyrazolonyl]-4,4′-methane has been synthesized from 1(2)-pyridyl-3-methyl-5-pyrazolone and hexamethylenetetramine. The structure has been proved by determination of the molecular weight and UV, IR and NMR spectra. The fluorescence spectra of aqueous solutions of the Tb- and Dy- and Sm-complexes, and the dependence of the relative fluorescence intensity on the pH-value, on the metal:reagent ratio and on other rare earth ions are shown. The determination of Dy(III) and Tb(III) in other rare earths is described.

Résumé—On a synthétisé le composé [bis 1(2)-pyridyl 3-méthyl 5-pyrazolonyl] 4,4′-méthane à partir de la 1(2)-pyridyl 3-méthyl 5-pyrazolone et de l'hexaméthylènetétramine. On a établi la structure par détermination du poids moléculaire et par les spectres UV, IR et RMN. On présente les spectres de fluorescence de solutions aqueuses des complexes avec Tb, Dy et Sm et la dépendance de l'intensité relative de fluorescence par rapport à la valeur du pH, au rapport métal: réactif et aux autres ions de terres rares. On décrit le dosage de Dy(III) et Tb(III) dans d'autres terres rares.

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ARSENAZO III AND ITS ANALOGUES—IV

THE ELECTRONIC STRUCTURE OF ARSENZO III IN MEDIA OF DIFFERENT ACIDITY

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Summary—By means of a single method, MOLCAO, the states of arsenazo III in strongly acidic, neutral and alkaline media has been studied. In the range from 1*N* sulphuric acid to pH 8, when the conjugated groups are not ionized the reagent is found in the azo form. Single stage ionization of the acidic (—OH, —NH—N=) or basic (—N_2—, =C=O) groups leads to a disruption of the symmetry of the system and to the appearance of the quinone-hydrazone form together with the azoide. The azoide and quinone hydrazone tautomers occur in the ratio 4:1 in concentrated sulphuric acid medium in and 22:3 alkaline medium.

WE HAVE proposed elsewhere the method MOLCAO for calculation of the π-electron structure and electronic spectra of complicated organic reagents,[1] and of the corresponding complexes with non-transition elements,[2] on the basis of which we examined a series of monoazo compounds. The same model was used[3] to examine arsenazo III, the properties of which have previously been described.[4] Hypotheses have been made[5,6] about the form of the reagent in various media, and its ionization constants have been determined,[7] but it is not possible to reach definite conclusions on the basis of a qualitative comparison of the absorption spectra and properties of the reagent in different media. This deficiency can be remedied by the use of MOLCAO.

EXPERIMENTAL

Arsenazo III was synthesized by the usual method.[6] Its absorption spectrum was measured on an SFD-2 spectrophotometer, for solutions in 95% and 0·1*N* sulphuric acid, at pH 9, and in 30% potassium hydroxide solution.[3,4] For attribution of the absorption bands to particular electronic transitions, the spectral curve was resolved into Gaussian curves.[8] We used the fact that one side of the absorption peak at longest wavelength is not distorted by overlap of neighbouring bands in regions where the absorbance (A) is low, since for points on this part of the curve, the graph of $\Delta \log A = f(\nu)$ is a straight line which gives $\nu(\mathrm{I})_{\max}$ as the intercept on the abscissa (Fig. 1*a*). The graph of the function $\log A = f'(\nu - \nu_{\max})^2$ must also be a straight line for the same absorbance values, its intercept on the ordinate giving the value of $A(\mathrm{I})_{\max}$ (Fig. 1*b*). By using the equation for the Gauss curve:

$$A = A_{\max} \,.\, \exp\left\{-\frac{(\nu - \nu_{\max})^2}{\Delta\nu_{1/2}^2} \,.\, \ln 2\right\} \tag{1}$$

where $\Delta\nu_{1/2}$ is the half-width of the band for $A = \frac{1}{2}A_{\max}$, we can find $\Delta\nu(\mathrm{I})_{1/2}$ from the given values of $A(\mathrm{I})_{\max}$ and $\nu(\mathrm{I})_{\max}$, and then construct band (I). On deducting this band from the spectrum we obtain a new contour. The long-wavelength slope of this curve does not give a linear dependence of curve is formed by overlap of several bands. For the region 17000–22000 cm^{-1} we can expect two bands, from the symmetry of the curve. By choosing parameters for the bands so that a straight line was obtained for the co-ordinates A/A_2 and A_3/A_2 (Fig. 1*c*), we were able to resolve the second and third bands (A is the total absorbance on the composite curve, and A_2 and A_3 the absorbances on the

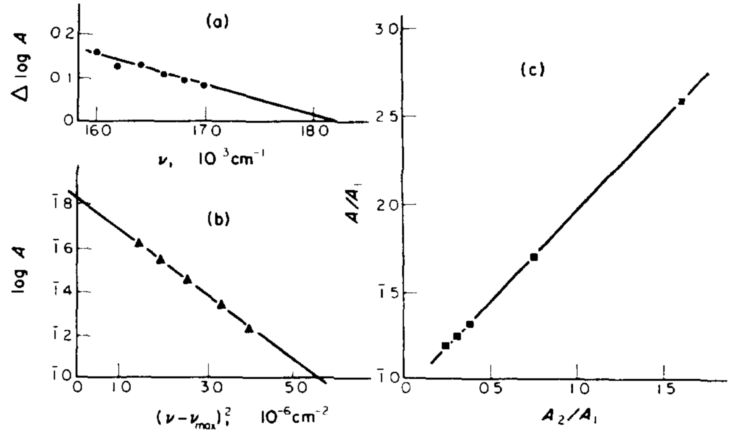


FIG. 1.—Determination of (*a*) ν_{max} and (*b*) A_{max} for band I of the absorption spectrum of arsenazo III in 0·1*N* sulphuric acid, and verification (*c*) of the accuracy of resolution of the two bands in Fig. 3.

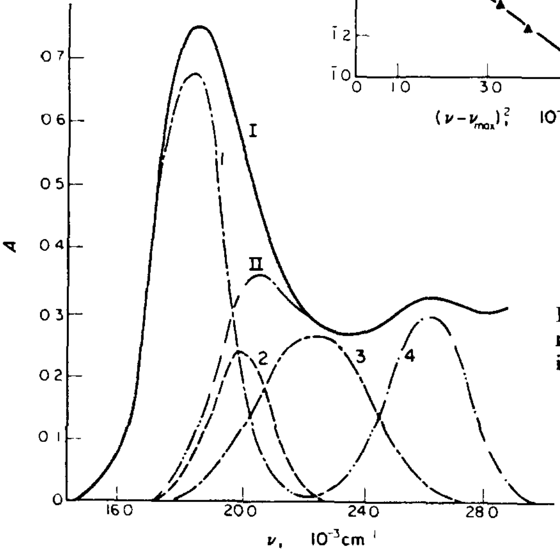


FIG. 2.—Absorption spectrum of arsenazo III resolved into Gaussian curves (1–4); band II is derived by subtracting curve 1 from band I.

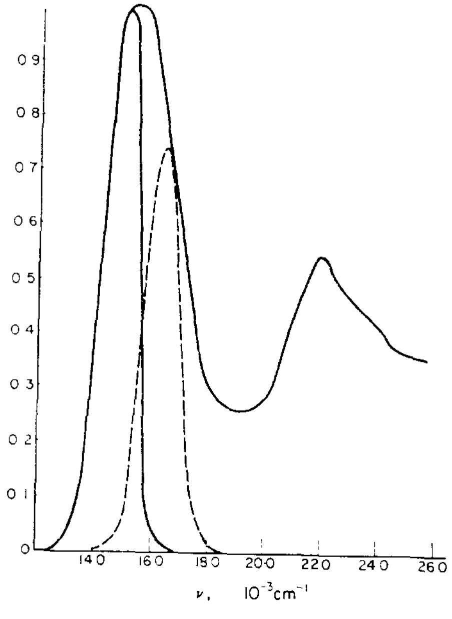


FIG. 3.—Absorption spectrum of arsenazo III in 95% sulphuric acid, resolved into two Gaussian curves.

second and third Gaussian curves respectively, The fourth band was resolved in the same way as the first. The spectrum of arsenazo III in 0·1N sulphuric acid, resolved in this way, is shown in Fig. 2. The corresponding spectral analyses for concentrated sulphuric acid medium and a solution at pH 9·0 are shown in Figs. 3 and 4.

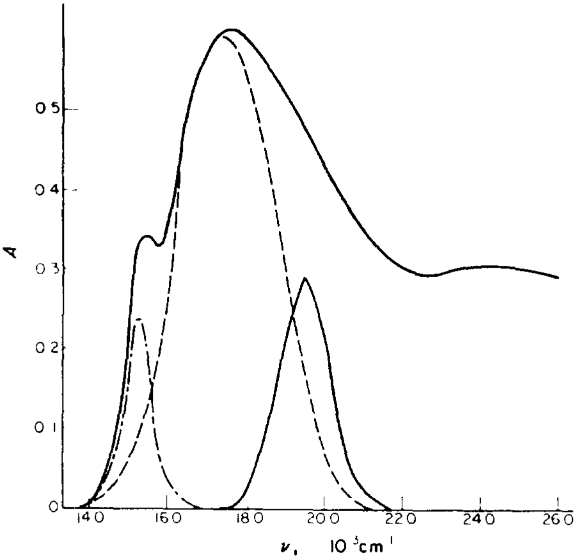


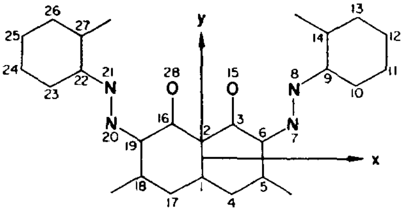
FIG. 4.—Absorption spectrum of arsenazo III at pH 9·0, resolved into three Gaussian curves.

CALCULATIONS AND RESULTS

The parameters ε_i, related to the energy levels E_i by the equation $\varepsilon_i = (\alpha - E_i)/\beta_0$, and the molecular orbital coefficient $C_k^{(i)}$ of the orbitals $\psi_i = \sum_k C_k{}^{(i)}\chi^{(k)}$ were found by solving the secular equations by a matrix method:

$$C_k{}^{(i)}(\varepsilon + \delta_k) + \sum_j h_{kj}C_j^{(i)} = 0 \qquad (2)$$

where $k = 1, 2, \ldots N$, and N is the number of π-centres. The sum is found of all j's contiguous to k. The choice of parameters* is δ_k and h_{ki}, and the non-coplanarity of the system is calculated in the same way as for arsenazo I.[2] The values of the parameters are given in Table I. For calculating the transition dipole moment we used the following coordinate system and method of numbering the atoms:



The bond angles were taken as 120° and the length of the C—C bonds as 1·39 Å. Other bond lengths were taken from the standard tables.[9] In view of the low non-planarity the P_z component of the transition dipole moment was taken as zero.

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* In English nomenclature δ_k is usually denoted by h and h_{kj} by k.

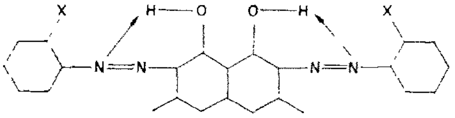
TABLE I.—VALUES OF PARAMETERS USED*

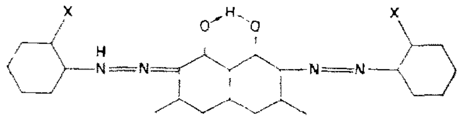
Atomic state	δ_k	h_{kj}	Atomic state	δ_k	h_{kj}
$\alpha\dagger_{c(as)}$	−0·05	0	$\alpha^{+}_{O=}$	2·50	2·00
$\alpha_{\overset{H}{\overset{\uparrow}{N}}=}$	0·58	0·97	α^{-}_{O-}	0·80	0·80
$\alpha^{+}_{-N=}$	2·00	1·00	$\alpha_{-\dot{N}=}$	0·63	1·00
$\alpha_{\ddot{O}-}$	2·00	0·90	$\alpha_{-\ddot{O}H\leftarrow}$	1·80	0·9

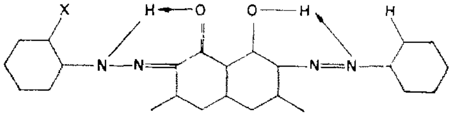
* Induction parameter = 0·1.

† Coulomb integral for the carbon atom adjacent to the arsenic atom.

Ionization of the sulphonic group was not taken into account,[2] and in acidic medium (0·1–1N sulphuric acid) the compound is un-ionized except for this grouping. It can therefore be described by means of the canonical structures I–III.


I


II


III

The asymmetric forms of I are less probable than the others. In Table II the theoretical and experimental data are given for the spectra of forms I–III; λ_{max} was calculated as before.[1] It can be seen that there is agreement between theory and experiment only for form I, so the reagent evidently exists in an azo form in media in which only the sulphonic or arsonic groups dissociate a proton (pH 1–8). In less polar solvents there is a maximum at 620–630 mμ, indicating emergence of a small amount of form II. Absorption bands in the 620–670 mμ region arise when the reagent is in either alkaline (pH 9–10) or very acidic (85% sulphuric acid) media, conditions in which the occurrence of both the azide and quinone–hydrazone ionized forms can be expected. This possibility, however, must be confirmed quantitatively.

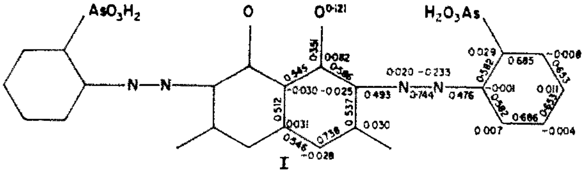
The molecular diagrams with charge densities and bond orders for the neutral reagent were calculated and are shown below. It can be seen that for the azo form I the most likely site for protonation is the nitrogen atom next to a benzene ring.

TABLE II.—CALCULATED AND EXPERIMENTAL ABSORPTION DATA FOR ARSENAZO III IN 0·1 N SULPHURIC ACID

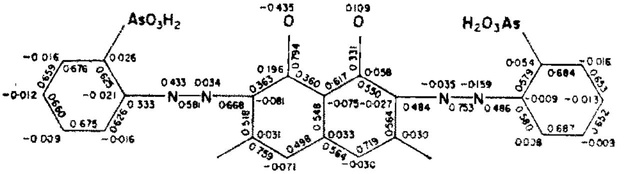
Canonical form	λ_{max}, mμ				$P_1{}^2\nu_1:P_2{}^2\nu_2:P_3{}^2\nu_3:P_4{}^2\nu_4$
	1	2	3	4	
I	543 (2·90)*	512 (0·24	418 (1·51)	400 (1·20)	1·00:0·08:0·63:0·53
II	622 (3·85)	—	456 (0·74)	412 (1·36)	1·00:0·00:0·26:0·53
III	672	472	438	—	—
Experimental values	538	500	446	385	$I_1:I_2:I_3:I_4$ 1·00:0·29:0·57:0·49

* Figures in brackets are squares of the transitional dipole moments.

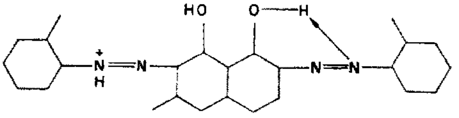
This nitrogen atom has the maximum negative charge. The carbonyl oxygen atom has similar properties for form II. Thus for strongly acidic media, just as with mono-azo compounds,[2] the structure of arsenazo III can be expected to be characterized by tautomeric equilibria of forms IV and V; a two-stage protonation leading to form VI can also be considered possible.



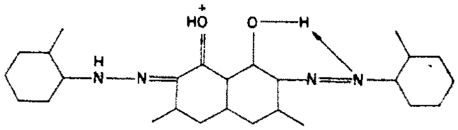
I



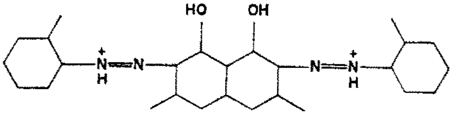
II



IV



V



VI

Calculation of the positions of λ_{max} of the longest wavelength absorption band of forms IV–VI gives the values 670, 620 and 570 mμ respectively. Comparison of these figures with those obtained by resolution of the spectrum of the reagent in concentrated sulphuric acid (Fig. 3) shows agreement for forms IV and V, so a two-stage protonation is unlikely. By estimation of the long-wave transition moments, the relative amounts of forms IV and V can be evaluated. Let x be the fraction of IV, and $(1 - x)$ that of V. The integrated intensity I_i of the ith Gaussian band is given by $I_i = k_i A_i \Delta\nu_i$, where A_i is the maximum absorbance in the band, $\Delta\nu_i$ is the bandwidth at half peak-height, and k_1 is a proportionality constant. The theoretical intensity of the band is given by $I_i = k_2 x_i P_i^2 \nu_i$ where P is the transitional dipole moment and k_2 is another proportionality coefficient. From the relationship

$$\frac{A_1\Delta\nu_1}{A_2\Delta\nu_2} = \frac{x\nu_1 P_1^2}{(1 - x)\nu_2 P_2^2} \tag{3}$$

we obtain

$$x = \frac{A_1\nu_2 P_2^2 \Delta\nu_1}{A_2\nu_1 P_1^2 \Delta\nu_2 + A_1\nu_2 P_2^2 \Delta\nu_1} \tag{4}$$

The results of estimations of the spectral characteristics of forms IV and V are given in Table III. From these results and the parameters obtained from Fig. 3 ($\Delta\nu_1 = 1{\cdot}6 \times 10^3$ cm^{-1}; $A_1 = 0{\cdot}98$; $\Delta\nu_2 = 1{\cdot}56 \times 10^3$ cm^{-1}; $A_2 = 0{\cdot}72$), use of

TABLE III.—CALCULATED AND EXPERIMENTAL ABSORPTION DATA FOR ARSENAZO III IN 95% SULPHURIC ACID.

Canonical form	$\lambda_{\max}$, $m\mu$				Conjugation energy, β_0
	1	2	3	4	
IV	671 (1·506)	483 (1·91)	458 (1·57)	373; 362 (0·143)(0·668)	12·7
V	622 (3·90)	487 (0·623)	437 (1·519)	366 (0·461)	12·0
Experimental values	676, 614	480–520	420–460	350–390	

equation (4) gives the ratio 4:1 for the azide and quinone-hydrazone forms. This result was confirmed by comparison of the ratio of the total integrated intensity of the first two of the long-wavelength bands to that of the others, calculated theoretically from the spectra. From the spectra we have

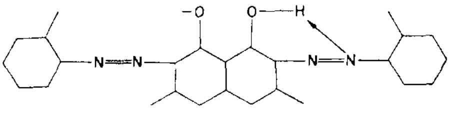
$$\frac{I_1 + I_2}{\sum\limits_{i=3}^{8} I_i} \sim 0{\cdot}5$$

and theoretically

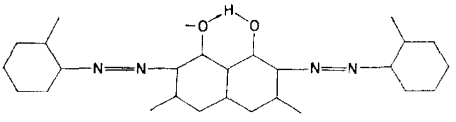
$$\frac{xP_1^2\nu_1 + (1 - x)P_2^2\nu_2^2}{\sum\limits_{i=3}^{8} x_i\nu_iP_i^2} \sim 0{\cdot}4.$$

Taking into account that there is a 5% error in determination of the parameters δ_k and h_{kj}, resulting in a 20% relative error in the square of the transition dipole moment, the agreement is reasonable and we can say that in concentrated sulphuric acid there is 3–4 times as much of form IV as of form V.

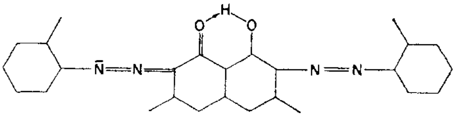
From the change in the spectrum when the pH is raised to 9 (Fig. 4) it can be assumed that a dissociation occurs. From the molecular diagrams it is clear that it must be the —OH group in form I or the —NH— group in form II, so forms VII–IX can be expected to result:



VII



VIII

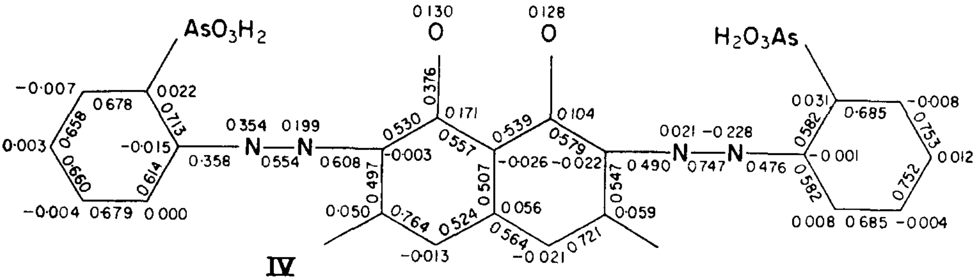


IX

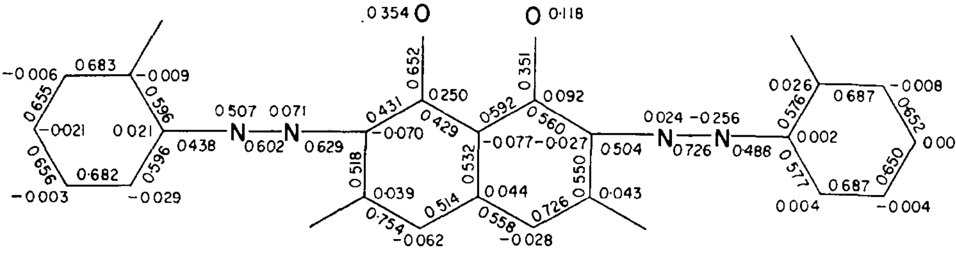
The calculated[1] spectral characteristics of the forms indicated are compared in Table IV with the experimental results (Fig. 4). It can be seen that the band at 655 mμ can be associated with form IX, and the remaining bands with form VIII, so we assume that at pH 9·0 there is tautomeric equilibrium between VIII, [88% according

TABLE IV.—CALCULATED AND EXPERIMENTAL ABSORPTION DATA FOR ARSENAZO III AT pH 9·0.

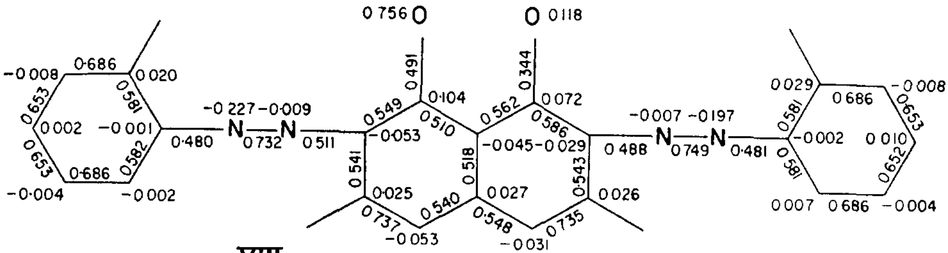
Canonical form	λ_{max}, $m\mu$				Conjugation energy, β_0
	1	2	3	4	
VII	626	545	433	346	—
VIII	586 (3·12)	526 (0·40)	416 (1·50)	385 (0·78)	11·7
IX	664 (3·73)	479 (0·993)	418 (1·62)	—	10·6
Experimental values	655, 570	513	430–380		



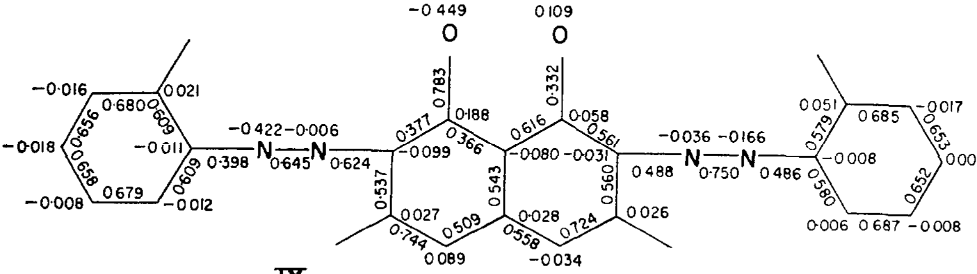
IV



V



VIII



IX

to equation (4)] and IX (12%). Confirmation was obtained from the ratio of the integrated intensities of the first three bands to that of the rest:

$$\frac{A_1\Delta\nu_1 + A_2\Delta\nu_2 + A_3\Delta\nu_3}{\sum\limits_{i=4}^{7} A_i\Delta\nu_i} = \frac{x_1{P_1}^2\nu_1 + x_2{P_2}^2\nu_2 + x_2{P_3}^2\nu_3}{\sum\limits_{i=4}^{7} x_i{P_i}^2\nu_i} \sim 1{\cdot}0.$$

The molecular diagrams of forms IV, V, VIII and IX are given on the previous page.

DISCUSSION

It was shown earlier[2,10] that for asymmetric monoazo compounds the quinone-hydrazone form always coexists with the azide form in solution. A special feature of the diazo compounds in moderately acidic media is the presence of only a symmetric azo form. In alkaline (pH 9·0–10·0) and strongly acidic media, ionization disrupts the symmetry and leads to appearance of the asymmetric quinone-hydrazone form alongside the azide. The possibility of coexistence of these two species is explicable on the basis of their π-electron structure. Examination of the molecular diagrams shows that for a reagent with un-ionized conjugated groups there are greater differences in the charge distribution and bond order, and that ionization perceptibly levels out these differences. The fact that the energy of the conjugated azo form always turns out to be much higher (Tables III and IV) determines the direction of displacement of the equilibrium.

These special features of arsenazo III determine its mode of reaction with metal ions. Two basic types of mechanism can be assumed. In one the metal interacts with the azo-oxy grouping, and in the other with the *peri*-dioxy grouping. The first type of reaction is characteristic of acidic media, and the second of neutral and alkaline media. Interactions of the metal with the quinone-hydrazone form of the reagent are also to be expected.

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Zusammenfassung—Die Struktur von arsenazo III in stark sauren, neutralen und alkalischen Medien wurde mit Hilfe eines einfachen Methode MOLKAO, berechnet. Im Bereich zwischen 1*N* Schwefelsäure und pH 8, wo die Konjugation Gruppen nicht ionisiert sind, liegt das Reagens in der Azoform vor. Einstufenionisation der sauren (—OH, —HN—N═) oder basischen (—N$_2$—, ═C═O) Gruppen führt zur Aufhebung der Symmetrie des Systems und dem Erscheinen der Chinonhydrazonform neben dem Azoid. Die Azoid- und Hydrazon-Tautomeren liegen in konzentrierter Schwefelsäure in Verhältnis 4:1, in alkalischem Medium im Verhältnis 22:3 vor.

Résumé—Au moyen d'un simple, method MOLKAO, on a etudice la structure de l'arsenzo III en milieux fortement acide, neutre et alcalin. Dans le domaine allant de l'acide sulfurique 1*N* à pH 8, lorsque les groupes conjugeé ne sont pas ionisés, on trouve le réactif sous la forme azoide. L'ionisation à un seul stade des groupes acides (—OH, —NH—N═) ou basiques (—N$_2$—, ═C═O) mène à une rupture de la symétrie du système et à l'apparition de la forme quinonehydrazone en même temps que de l'azide. Les tautomères azoide et hydrazone se trouvent dans le rapport 4:1 en milieu acide sulfurique concentré et 22:3 en milieu alcalin.

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ANALYSIS OF NIOBIUM ALLOYS

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Summary—An ion-exchange method was applied to the analysis of synthetic mixtures representing various niobium-base alloys. The alloying elements which were separated and determined include vanadium, zirconium, hafnium, titanium, molybdenum, tungsten and tantalum. Mixtures containing zirconium or hafnium, tungsten, tantalum and niobium were separated by means of a single short column. Coupled columns were employed for the resolution of mixtures containing vanadium, zirconium or titanium, molybdenum, tungsten and niobium. The separation procedures and the methods employed for the determination of the alloying elements in their separate fractions are described.

IN RECENT years refractory-base alloys for high temperature applications have become increasingly prominent. Niobium-base alloys containing V, Zr, Hf, Ti, Mo, W and Ta in various combinations are typical of such materials. Mutual interference due to chemical similarity and marked differences in the hydrolytic behaviour of these elements seriously complicate the analysis of such mixtures by conventional chemical means.

The analysis of such mixtures can be greatly simplified by separating the elements from each other before their determination. Ion-exchange chromatography has been the most successful separation technique for this group of elements.[1,2,3] However, existing methods do not provide for the separation of vanadium, and they are not applicable to the complete resolution of mixtures containing two or more of the elements titanium (or zirconium), molybdenum and tungsten in the presence of large amounts of niobium.[4]

A study performed in this laboratory has led to the development of an ion-exchange method which provides for the complete resolution of such mixtures. This method differs from others[1,2,3] by employing hydrofluoric acid alone, rather than mixtures of hydrochloric and hydrofluoric acids, for the initial separations of vanadium, titanium (or zirconium), and molybdenum. In this way, interference from large amounts of niobium is avoided and provision can be made for the separate elution of vanadium. Thus, the ion-exchange method developed in this laboratory should be applicable to the analysis of niobium alloys in general, and the object of the work reported here was to evaluate this method. Of the alloying elements usually present in niobium alloys, only hafnium and tantalum were not included in the original ion-exchange study. No difficulty was expected with hafnium since published data clearly indicated that hafnium would behave like zirconium and titanium in the separation scheme,[5] and these elements would be eluted together in the same fraction. The same is true of methods using hydrochloric–hydrofluoric acid mixtures as eluents.[1,2,3] Only one of these elements was present in each of the mixtures analysed in the present work.

Tantalum, like niobium, is very strongly adsorbed from hydrofluoric acid and the hydrochloric–hydrofluoric acid mixture used in the proposed method,[5,6] and should remain on the column with niobium while the other elements are removed. These two elements could then be readily separated by an established procedure.[7]

Because suitable standard samples were not available, synthetic standards were prepared by taking appropriate amounts of the pure metals. Samples simulating three commercially available niobium-base alloys (types C-129, FS-85 and B-66) and samples simulating complex niobium-base alloys of varying composition (containing vanadium, titanium, molybdenum and tungsten) were analysed by the proposed method. In addition, an FS-85 alloy sample was tested in conjunction with an inter-laboratory testing programme.

EXPERIMENTAL

Ion-exchange columns

Polystyrene tubing 1 in. in diameter was used to prepare the columns. The bottom of the tubing was closed with a neoprene stopper with a ¼-in. hole. A 3-in. length of stiff polyethylene tubing (¼-in. outside diameter and ⅛-in. bore) was inserted into the hole flush with the upper surface of the stopper. A piece of Tygon R tubing was attached to the polyethylene tube and the flow controlled by a hose clamp on the Tygon tubing. The bottom of the large polystyrene tube was covered with a layer of vinyl chloride plastic "wool" as a support for the resin bed. The column was filled with 270-mesh Dowex-1 ion-exchange resin of 8–10% cross-linkage to obtain a settled resin column of the desired height, 4 or 8 in. The dry resin was added as a slurry in hydrochloric acid (1 + 9). A layer of the acid-resistant fibre was placed on top of the resin bed to avoid disturbance during addition of sample and eluent. The polystyrene tubing was long enough to give at least a 2-in. clearance above the resin bed. Eluent was added from plastic bottles 3 ft. above the column, *via* Tygon tubing and a 3-in. length of polyethylene tubing inserted through a ¼-in. hole in a neoprene stopper in the top of the column. Flow-rate was controlled by a hose clamp on the Tygon tubing.

Preparation of synthetic samples

Weighed amounts of the pure metals were transferred to a covered Teflon beaker and treated with 10 ml of hydrofluoric acid. When chemical reaction subsided nitric acid was added dropwise, each addition being made only after the reaction had subsided. When further addition of nitric acid no longer produced vigorous reaction, the samples were diluted with 10 ml of water and heated to complete dissolution. In the case of samples containing vanadium and/or molybdenum, additional nitric acid was added as needed to dissolve these metals.

The solutions were evaporated to dryness on a steam-bath, and the residues were dissolved in 75 ml of 6*M* hydrofluoric acid while still on the steam-bath. When clear solutions were obtained the samples were allowed to cool before the ion-exchange separation. With the exception of the FS-85 alloy mixture each sample weight totalled approximately 1 g. The FS-85 samples were made up to a total weight of about 0·5 g.

Ion-exchange separations

It has been shown that up to 100 mg of zirconium and tungsten can be separated from each other and from a relatively large amount (800 mg) of niobium by using 27·5*M* hydrofluoric acid to separate zirconium on a 4-in. column of strong-base anion-exchange resin. Tungsten can then be cleanly separated from niobium[1,2] without fear of niobium contaminating the tungsten fraction, which often occurs when hydrochloric–hydrofluoric acid mixtures are used at the outset. This method (Scheme A, below) was used for the analysis of the C-129 and FS-85 type mixtures.

Because the elution characteristics of vanadium, titanium and zirconium are practically identical in 27·5*M* hydrofluoric acid, the resolution of mixtures containing vanadium and zirconium (or titanium) requires a different scheme. Up to 100-mg amounts of vanadium and zirconium (or titanium) can be separated in the presence of a large amount of niobium (800 mg) by eluting vanadium first through an 8-in. column with 13*M* hydrofluoric acid. When molybdenum is also present, however, a larger column (at least 12 in.) must be used in order to make possible the subsequent separation of zirconium (or titanium) and molybdenum with 27·5*M* hydrofluoric acid. With such a long column, excessively large fraction volumes must be collected, especially for the initial elution of vanadium, and the separations take a long time.

A more efficient system of coupled columns was therefore devised. Vanadium is first eluted through an 8-in. column with 13*M* hydrofluoric acid. Then a 4-in. column is attached to the bottom of the first column, and zirconium (or titanium) and molybdenum are eluted in separate fractions with 27·5*M* hydrofluoric acid. The columns are then separated and tungsten, if present, is eluted from the 4-in. column while niobium is simultaneously removed from the 8-in. column. This method (Scheme B below) was used for the analysis of the B-66 alloy type mixtures and the simulated complex alloys.

Scheme A

Condition a 4-in. column by passing 100 ml of 6*M* hydrofluoric acid through it in 25-ml increments. Transfer the sample to the column and drain it into the resin. Wash the sample beaker and top of the column with 25 ml of 6*M* hydrofluoric acid. Close the hose clamp when the washings have drained to the top of the resin bed. Discard the effluent and connect the eluent supply line to the column. Add the first eluent, 27·5*M* hydrofluoric acid, to give an inch depth of it above the resin. Open the hose clamp at the bottom of the column and drain the solution to the top of the resin, catching the eluate in a clean plastic beaker. Pass the eluent through the column at a flow-rate of 3 ml/min, keeping an inch of solution above the resin. Collect 175 ml of eluate, stop the flow, and drain the solution to the top of the resin. Use this fraction for the determination of zirconium or hafnium.

Wash the column with two 15-ml portions of the second eluent, 7*M* hydrochloric acid—3*M* hydrofluoric acid solution, draining each to the top of the resin bed (to minimize intermixing of the successive eluents). Elute with the second eluent in the same way as with the first. Collect 150 ml of eluate for tungsten determination and change to the next eluent as before.

Elute niobium with 200 ml of 3*M* ammonium chloride—1*M* hydrofluoric acid solution and finally elute tantalum with 300 ml of 3*M* ammonium chloride—1*M* ammonium fluoride solution.

Condition the column with 100 ml of 6*M* hydrofluoric acid to prepare it for the next sample.

Scheme B

Prepare and condition a 4-in. and an 8-in. column as in Scheme A, using 150 ml of 6*M* hydrofluoric acid for the 8-in. column.

Transfer the sample to the 8-in. column as described in Scheme A but do not discard any effluent [any vanadium(IV) present is only slightly adsorbed]. Elute vanadium with 13*M* hydrofluoric acid and collect 800 ml of eluate, including the volume of sample and washings (about 100 ml). Stop the flow of eluent and drain the solution to the top of the resin.

Into the top of the 4-in. section fit a stopper with a short piece of polyethylene tubing inserted through it and attach it to the bottom of the 8-in. section by means of a short piece of Tygon tubing.

Wash the coupled columns with two 15-ml portions of 27·5*M* hydrofluoric acid, draining each to the top of the resin. Then elute with 27·5*M* hydrofluoric acid at maximum flow-rate (~2 ml/min). Collect 350 ml of eluate for zirconium or titanium determination, and stop the flow.

Continue the elution and collect a second fraction (250 ml) for determination of molybdenum. Close all the hose clamps, including one placed on the Tygon tubing connecting the sections, and disconnect the columns.

Elute tungsten from the 4-in. section with 225 ml of 7*M* hydrochloric acid–3*M* hydrofluoric acid solution, and at the same time elute niobium from the 8-in. section with 300 ml of 3*M* ammonium chloride–1*M* hydrofluoric acid solution.

Condition the columns with 6*M* hydrofluoric acid to prepare them for the next sample.

In the application of these separation schemes, especially Scheme B, it is necessary that the recommended experimental conditions such as resin particle size, flow-rate, and fraction volumes, be used. For example, increased flow-rate results in less efficient elution and wider elution bands. Conversely, decreased flow-rate provides more efficient elution and consequently narrower elution bands. Thus, if the flow-rate is changed, the effect on the elution behaviour of the elements must be evaluated and the fraction volumes adjusted accordingly. Too fast a flow-rate may cause overlapping of the elution bands so that quantitative separations cannot be achieved. Larger resin particle size affects behaviour in the same direction as increased flow-rate: elution efficiency is decreased and elution bands are broadened.

Chemical Determination of Separated Constituents

Vanadium

Determine vanadium by titration with potassium permanganate.[8] Transfer the vanadium fraction to a Teflon beaker, add 20 ml of sulphuric acid (1 + 1) and 5 ml of nitric acid, and evaporate on a hot-plate till sulphur trioxide fumes appear. Cool, transfer the residue to a Pyrex beaker with adequate washing, evaporate, then heat to strong fumes for 2–3 min. Cool, dilute the solution to ~100 ml and cool again in a water-bath. Add 5% potassium permanganate solution dropwise until the solution remains pink for at least 10 min. Add 3·3 ml of 0·06*N* ferrous ammonium sulphate for each 1% of vanadium expected (1-g sample) and 13 ml excess*; oxidize the excess with 15 ml of 15% ammonium persulphate solution. Titrate vanadium(IV) with 0·06*N* potassium permanganate to a pink end-point.

Zirconium

Gravimetric method.[9] Transfer the zirconium fraction to a Teflon beaker, add 20 ml of sulphuric acid (1 + 1) and 5 ml of nitric acid, and evaporate till fumes appear. Cool, transfer the solution to a Pyrex beaker, add 1 ml of nitric acid, evaporate till fuming and heat for 2–3 min. more. Cool, dilute the solution with 80–90 ml of water and add 1–2 ml of hydrogen peroxide (30%) and 25 ml of diammonium phosphate solution (30%). Heat gently for 1 hr and then allow to stand overnight. Add paper pulp and filter through a close-texture paper containing a little pulp. Wash the precipitate 18–20 times with ammonium nitrate solution (5%), and ignite it in a weighed platinum crucible, first at low temperature to remove carbon and finally at 1050° for 20 min. The conversion factor is 0·344.

Photometric method.[10] Treat the zirconium fraction as before, but after the second fuming add 27·5 ml of concentrated sulphuric acid, transfer the solution to a 500-ml volumetric flask, cool, and dilute to volume with water. Transfer a 10-ml aliquot to a 100-ml volumetric flask and dilute to volume. Transfer a 20-ml aliquot of this solution to a 25-ml volumetric flask, add 1·5 ml of 0·05% Xylenol Orange solution, dilute to volume, mix, and measure the absorbance in a 1-cm cell at 535 mμ, using a reagent blank as reference. Prepare a calibration curve to cover the range 10–60 μg of zirconium, adding 2·0 ml of 2·5*N* sulphuric acid to each standard.

A stock zirconium solution can be prepared by dissolving ~0·6 g of zirconyl nitrate dihydrate in 200 ml of hydrochloric acid (1 + 1) and diluting to 1 litre, and standardized gravimetrically with *p*-chloromandelic acid[11] or cupferron. The standard solution for calibration is prepared by diluting the stock solution 10-fold.

Titanium

Transfer the titanium fraction to a Teflon beaker, and heat to fuming with 20 ml of dilute sulphuric acid (1 + 1) and 5 ml of nitric acid added as for the zirconium fraction. Dilute the solution to 100 ml in a volumetric flask. Take an aliquot containing 1–2 mg of titanium for the photometric determination as the peroxide complex,[9] and dilute it to volume in a 100-ml volumetric flask with dilute sulphuric acid (1 + 9). With a clean dry pipette remove 25 ml of this solution to use as reference solution for the photometric measurements. To the remainder add 1·0 ml of hydrogen peroxide (30%) and mix. Measure the absorbance in a 1-cm cell at 410 mμ.

Prepare a calibration curve covering the range 0·5–2·5 mg of titanium, using the same procedure as for the samples. A standard titanium solution (0·25 mg/ml) can be made by dissolving 419 mg of pure titanium dioxide in a mixture of 25 ml of sulphuric acid and 10 g of ammonium sulphate and diluting to 1 litre with sulphuric acid (1 + 9).

Hafnium

Determine hafnium gravimetrically by precipitation with cupferron and ignition to the oxide.[12] Heat the hafnium fraction with 40 ml of sulphuric acid (1 + 1) and 5 ml of nitric acid in a Teflon beaker till fumes appear. Transfer to a Pyrex beaker and fume strongly for 2–3 min. Cool and dilute with 180 ml of water, then cool again to 5–10° in an ice-bath. Precipitate the hafnium with 50 ml of cold 6% cupferron solution, and let stand for 30 min in the ice-bath with intermittent stirring. Then filter off on medium porosity paper and wash the precipitate with cold cupferron wash solution (100 ml of hydrochloric acid and 25 ml of the cupferron solution, diluted to 1 litre). Ignite to the oxide in a weighed platinum crucible, at 1000° for 1 hr. The conversion factor is 0·848.

Molybdenum

Determine molybdenum photometrically as the thiocyanate complex.[13] Transfer the molybdenum fraction to a Teflon beaker and heat it with 5 ml of nitric acid and 5 ml of perchloric acid till light fumes appear, cool, and transfer to a Pyrex beaker. Add 1 ml of nitric acid, fume strongly for 5 min, cool, then transfer the solution to a 500-ml volumetric flask and dilute to volume. Transfer to a 100-ml volumetric flask an aliquot containing from 0·1 to 1·0 mg of molybdenum and add 17 ml of perchloric acid containing 2·5 g of iron per litre. Heat the solution to strong fumes, cool it somewhat, dilute with 25 ml of water and mix. Cool the solution to room temperature and add, with swirling, a mixture of 20 ml of tin(II) chloride solution (25% in 2*M* hydrochloric acid) and 10 ml of 10% sodium thiocyanate solution. Dilute to volume, mix, and measure the absorbance at 515 mμ against a reagent blank.

* About 3 ml to reduce the excess of permanganate and 10 ml to allow a tolerance of about +3% on the amount of vanadium present.

A standard molybdenum solution (~1 mg/ml) for calibration purposes can be prepared by dissolving 186 mg of ammonium heptamolybdate tetrahydrate in water and diluting to 1 litre, and standardized by precipitating the molybdenum as silver molybdate.

Tungsten

Determine tungsten gravimetrically as tungstic oxide.[14] Transfer the tungsten fraction to a Teflon beaker and heat to strong fumes with 20 ml of dilute sulphuric acid (1 + 1). Cool and transfer to a Pyrex beaker. Dissolve any precipitate remaining in the Teflon beaker by adding a few ml of water and a sodium hydroxide pellet, and add it to the Pyrex beaker. Add 5 ml of nitric acid and again heat to strong fumes. Cool, dilute to 160 ml, add 15 ml of nitric acid and boil for 15–20 min. Add paper pulp and let stand at room temperature for several hours. Filter off on close-textured paper to which paper pulp has been added, transferring and washing the precipitates with warm hydrochloric acid (1 + 49). Ignite at 800° to constant weight in a weighed platinum crucible. The factor is 0·793.

Tantalum

Determine tantalum gravimetrically by precipitation with cupferron and ignition to the pentoxide.[9] Transfer the tantalum eluate to a Pyrex beaker containing 10 g of boric acid and 55 ml of concentrated hydrochloric acid. Heat to dissolve the boric acid, then cool in an ice-bath to 5–10°. Add 50 ml of cold 6% cupferron solution and paper pulp and keep the solution in the ice-bath for 15–20 min with intermittent stirring. Filter off on medium porosity paper and wash with the same cupferron wash solution as for hafnium. Ignite to constant weight at 1000° in a weighed platinum crucible. The factor is 0·819.

RESULTS AND DISCUSSION

Analysis of synthetic samples

The results in Table I show that the proposed ion-exchange method gives quantitative recovery of each of the alloying elements determined. Vanadium, molybdenum and tungsten were determined in the range 2–10% with average deviations of 0·03, 0·04 and 0·03% respectively. The average deviation for zirconium at the 1% level is 0·02%, while that for titanium in the range 1·5–5% is 0·05%. The values for hafnium at the 10% level and tantalum at the 27% level are 0·06 and 0·1%, respectively. It can be concluded, therefore, that the recommended procedure can be applied to niobium alloys in general for the determination of these alloying elements at levels of 10% or less, with a 1-g sample. Because of its strong adsorption, it should be possible to determine tantalum without difficulty at levels well above 27%. To determine tantalum in a 1-g sample at levels above 15%, appropriate aliquots of the tantalum-bearing eluate should be taken for the cupferron precipitation to avoid unwieldy amounts of precipitate. In that case, the eluate is heated with 10 g of boric acid and 75 ml of concentrated hydrochloric acid till the boric acid has dissolved, and after cooling is diluted to volume in a 500-ml volumetric flask. A 50-ml aliquot is diluted with 50 ml of hydrochloric acid (1 + 6) and precipitation is carried out as before.

For determination of the other alloying elements at levels above 10%, the sample size should be reduced to contain no more than 100 mg of each of the elements to be determined.

Analysis of a commercial FS-85 niobium alloy

The results obtained on the commercial FS-85 alloy are summarized in Table II. It was analysed three times, on different days, by Scheme A, 1-g samples being used because of the low zirconium content. The tantalum method was modified accordingly as described above.

TABLE I.—ANALYTICAL RESULTS OBTAINED BY RECOMMENDED PROCEDURES ON SYNTHETIC MIXTURES

C-129 Alloy type

	Hafnium, %		Tungsten, %	
Sample	Added	Found	Added	Found
1	10·42	10·40	10·00	9·96
2	10·13	10·09	9·98	9·96
3	9·87	9·76	9·87	9·81

FS-85 Alloy type

	Zirconium, %		Tungsten, %		Tantalum, %	
Sample	Added	Found*	Added	Found	Added	Found
1	1·13	1·10	10·33	10·41	26·7	26·7
2	1·10	1·12	10·29	10·31	26·8	26·9
3	1·01	0·98	10·19	10·19	26·9	27·1

B-66 Alloy type

	Vanadium, %		Zirconium, %		Molybdenum, %	
Sample	Added	Found	Added	Found†	Added	Found
1	5·14	5·07	1·13	1·12	4·90	4·92
2	4·60	4·57	1·09	1·09	4·64	4·65
3	4·95	4·95	1·68	1·63	4·57	4·49
4	5·19	5·16	1·14	1·17	4·82	4·78

Samples simulating complex alloys of varying composition

	Vanadium, %		Titanium, %		Molybdenum, %		Tungsten, %	
Sample	Added	Found	Added	Found	Added	Found	Added	Found
1	5·31	5·28	5·00	4·92	4·88	4·83	4·92	4·91
2	9·82	9·75	1·52	1·48	9·43	9·32	9·42	9·45
3	2·04	2·07	2·07	2·04	2·12	2·11	1·96	1·94
4	2·41	2·41	1·96	1·91	1·98	2·00	4·86	4·86

* Gravimetric.
† Photometric.

TABLE II.—ANALYTICAL RESULTS OBTAINED BY THE RECOMMENDED PROCEDURE ON A COMMERCIAL FS-85 ALLOY

Sample	Zirconium*, %	Tungsten, %	Tantalum, %
1	0·91	10·00	27·7
2	0·92	10·04	27·7
3	0·91	10·07	28·1
Average	0·91	10·04	27·8

* Determined by the gravimetric phosphate method.

This FS-85 alloy was the only niobium-base alloy tested in an inter-laboratory testing programme of refractory metal standards for the Materials Advisory Board Refractory Metals Sheet Rolling Sub-panel on Analytical Methods of the National Academy of Sciences and National Research Council. Fourteen laboratories participated in the determination of the alloying elements in this alloy. Analyses were performed by different techniques in accordance with individual laboratory preference. Many used X-ray fluorescence and emission spectroscopy, while others used wet chemical methods. Of the latter, the ion-exchange technique was predominant.

Although details of the methods employed by the various laboratories are not available, it is very likely that hydrochloric–hydrofluoric acid mixtures were used as eluents in the ion-exchange methods by the other laboratories. At least one laboratory with considerable experience in ion-exchange analysis is known to have eluted zirconium and tungsten together in the same fraction. This was done to avoid the contamination of tungsten with niobium, which generally occurs when attempts are made to separate zirconium and tungsten from each other with this system in the presence of a relatively large amount of niobium.

Average results from the individual laboratories and a statistical analysis are shown in Table III. The results were obtained from a final report on the refractory metals co-operative analysis programme.[15] Ion-exchange results are listed under chemical methods. The first figures listed for each element under this group are those reported by the present author. The few results obtained by wet chemical methods not involving ion-exchange are indicated.

TABLE III.—RESULTS OBTAINED ON FS-85 ALLOY, CLASSIFIED BY METHOD

	X-ray fluorescence			Emission spectroscopy			Chemical		
	Ta, %	W, %	Zr, %	Ta, %	W, %	Zr, %	Ta, %	W, %	Zr, %
	27·26	9·98	1·05	26·35	10·23	0·94	27·8	10·04	0·91
	27·9	10·1	0·87	28·62	10·53	0·91	28·82	10·0	0·92†
	30·3	11·6	1·12	27·45	11·59	1·54	27·73	9·86	0·95
	31·3	12·6	1·04				26·8	9·75	0·76
	26·9	10·3	0·80				27·46	10·22*	0·46
								10·2*	
Average	28·73	10·92	0·98	27·47	10·77	1·13	27·72	10·01	0·80
Average deviation	1·65	0·95	0·11	0·76	0·53	0·28	0·51	0·14	0·15
Standard deviation	1·95	1·14	0·135	1·14	0·72	0·37	0·78	0·19	0·20

* Tungsten determined by dithiol extraction–photometric method.

† Zirconium determined by phosphate precipitation following a fluozirconate separation.

These results are indicative of the sad state of affairs which exists in connection with the analytical determination of alloying elements in refractory alloys. The ion-exchange data for tantalum and especially for tungsten show better inter-laboratory agreement than do the results obtained instrumentally. On the other hand, the X-ray fluorescence values for zirconium show less scatter than those obtained by emission spectroscopy or chemical methods.

A summary of selected results, obtained after eliminating three outlying figures for each alloying element, also appeared in the final report.[15] The averages and standard deviations were: tantalum, 27·67% ± 0·67%; tungsten, 10·11% ± 0·22%; zirconium, 0·92% ± 0·092%.

These average values are in good agreement with the results obtained by the ion-exchange method proposed here. It should be noted, however, that the selected results still reflect considerable scatter, as indicated by the coefficients of variation which are 2·4%(Ta), 2·2%(W), 10%(Zr.).

Application of the proposed ion-exchange method to a series of synthetic niobium alloy standards yielded quantitative recovery of each of the elements determined. Although inter-laboratory testing results are available for only the FS-85 alloy, the wide divergence of the values reported by the individual laboratories for this alloy is ample evidence that there is a definite need for a reliable method suitable for the determination of alloying elements in niobium alloys. The method proposed here fulfills this need. In addition, the proposed method, unlike other ion-exchange methods, is especially well suited for application to the analysis of niobium alloys in general, since it provides for the separation of vanadium, molybdenum and tungsten from each other and from zirconium, titanium, or hafnium, without interference from large amounts of niobium.

Zusammenfassung—Zur Analyse synthetischer Mischungen, die verschiedenen Legierungen auf Niob-Basis entsprechen, wurde ein Ionenaustauschverfahren verwendet. Die abgetrennten und bestimmten Legierungselemente umfaßten Vanadium, Zirkonium, Hafnium, Titan, Molybdän, Wolfram und Tantal. Mischungen aus Zirkonium oder Hafnium, Wolfram, Tantal und Niob wurden mit einer kurzen Säule getrennt. Kombinierte Säulen wurden gebraucht zur Auftrennung von Gemischen aus Vanadium, Zirkonium oder Titan, Molybdän, Wolfram und Niob. Die Trennverfahren und die zur Bestimmung der Legierungselemente in ihren Fraktionen verwendeten Bestimmungsmethoden Werden beschrieben.

Résumé—On a appliqué une méthode d'échange d'ions à l'analyse de mélanges synthétiques représentant divers alliages à base de niobium. Les éléments d'alliages que l'on a séparés et déterminés comprennent: vanadium, zirconium, hafnium, titane, molybdène, tungstène et tantale. Des mélanges contenant: zirconium ou hafnium, tungstène, tantale et niobium ont été séparés au moyen d'une seule colonne courte. On a utilisé des colonnes couplées pour la résolution de mélanges contenant: vanadium, zirconium ou titane, molybdène, tungstène et niobium. On décrit les procédés de séparation et les méthodes employées pour la détermination des éléments d'alliages dans leurs fractions séparées.

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MASS SPECTROMETRIC ANALYSIS OF HIGH-PURITY CARBON DIOXIDE

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Summary—A high-vacuum, low-temperature, continuous separation technique has been used in conjunction with a mass spectrometer for the analysis of carbon dioxide containing vpm amounts of H_2, He, CH_4, Ne, N_2, CO, O_2 and Ar. The method relies on the condensation of carbon dioxide on the walls of a glass U-tube, cooled in liquid nitrogen, connected between an inlet and the ion source. A high-pressure carbon dioxide sample thus enters the inlet leak but only the impurities pass through the U-tube and reach the ion source, resulting in considerable gain in sensitivity and elimination of interference from carbon dioxide. The sensitivity of the method is several orders of magnitude better than the normal mass spectrometric method.

A NEED has arisen in recent years for high-purity carbon dioxide, necessitating the development of analytical methods capable of determining the permanent gas impurities at vpm levels. The only facilities available at these laboratories for analysis of high-purity gases are gas chromatography and mass spectrometry. An obvious initial choice of method is gas chromatography using a helium ionization detector.[1] This would offer adequate sensitivity for most of the impurities, except of course for helium, but difficulty would be experienced in attempting to separate H_2, Ne, O_2, Ar, CO, N_2 and CH_4 on any single column. Although highly activated molecular sieve 5A can be used[2] to separate O_2 and Ar, and to obtain partial separation of H_2 and Ne, in our experience a highly activated column of this nature increases the retention time for carbon monoxide and reduces the overall sensitivity of the chromatograph to this gas. The determination of impurities in carbon dioxide by normal mass spectrometric analysis techniques is limited because of the interference of a number of ion species, including CO^+ and O_2^+, which are produced in the ion source. The interference of the CO^+ ion with the nitrogen determination is extremely severe, the peak at m/e 28 in the spectrum of carbon dioxide being of the order of 8% of the parent peak. In order to be able to carry out a mass spectrometric analysis (particularly for traces of nitrogen) an impurity concentration or separation technique is required.

This report is concerned with the development of a high-vacuum, low-temperature, separation technique for use with a mass spectrometer (A.E.I. Model MS2G) for the analysis of high-purity carbon dioxide.

EXPERIMENTAL

Sample inlet system

It was considered that the simplest and most effective way of separating the impurities from the carbon dioxide sample, and at the same time gaining considerable sensitivity, was to admit continuously a high-pressure sample of carbon dioxide, *via* a direct inlet system,[3] into the mass spectrometer source inlet tube and then to remove the carbon dioxide by freezing it at 77°K, hence allowing only the volatile impurities to enter the ion source. A system was devised comprising an inlet valve, a condensation tube and a vacuum lock which allowed the instrument to be used in its normal configuration when required (Fig. 1). The vacuum lock valve (V_L), which is similar in construction to a normal A.E.I. inlet leak valve,[4] is constructed of brass and has a polished stainless steel insert for the valve seat. The inlet leak assembly is shown in Fig. 2, the leak being a 1-cm length of 0·01-mm bore Veridia glass capillary.

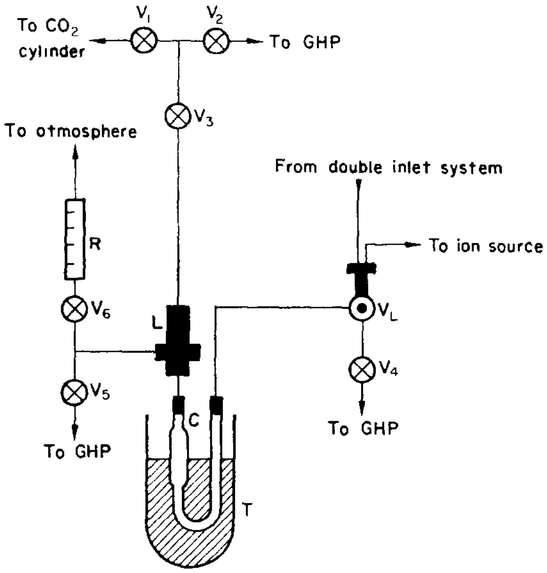

FIG. 1.—Schematic diagram of gas inlet system and vacuum lock assembly

V_1	1/16 in. Edwards needle valve
V_2, V_3, V_4, V_5, V_6	Edwards Saunders 1/4 in. valve.
V_L	Vacuum lock valve.
R	Rotameter (0·1–1·0 l./min).
C	Condensation tube
T	Liquid nitrogen trap
L	Sample inlet leak assembly
GHP	Gas handling plant

The condensation tube (Fig. 3) was constructed of glass, since preliminary work had indicated that materials such as stainless steel tended to adsorb atmospheric components.

Performance of the analysis system

The change in the impurity levels which could occur during carbon dioxide condensation was investigated by continuously sampling a blend of carbon dioxide containing 2 vpm each of H_2, He, O_2 and Ar, and 10 vpm of N_2 + CO over a period of several hours whilst the carbon dioxide layer was building up in the condensation tube. The sample was analysed at intervals and the results showed that no significant change occurred in the recorded ion beams over a period of 15–415 min. Hence, providing that the instrument is calibrated with standard gas mixtures over the desired impurity ranges, any permanent sorption of impurities will be automatically compensated for when constructing calibration curves.

In order to check the response time of the instrument, impurities were introduced into a stream of high-purity carbon dioxide, one at a time, and the times taken for the ion beams to stabilize were noted, Table I.

From these results it was decided to fix the minimum conditioning time for the instrument at 20 min, so that all the impurity ion beams have stabilized before an analysis is carried out on the gas leaving the condensation tube.

The precision of the method was determined by using a number of blends of carbon dioxide, containing all the previously mentioned impurities, prepared in gas cylinders at 500 psig, and the procedure described below.

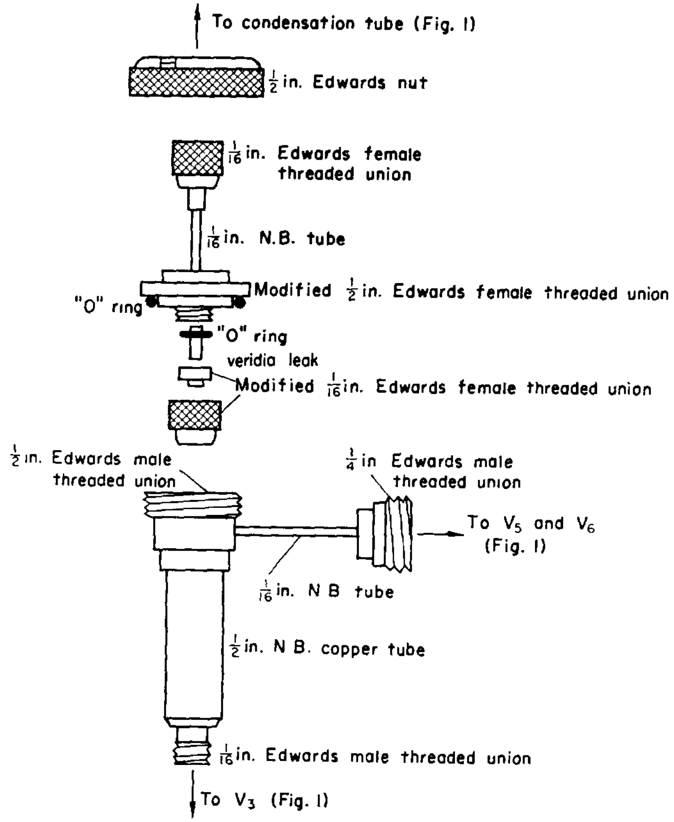

FIG. 2.—Sample inlet leak assembly (exploded diagram).

Procedure

Connect the carbon dioxide cylinder, *via* a gas regulator, to V_1. (If the cylinder is a siphon cylinder or it is required to analyse a liquid carbon dioxide sample, a vaporizer should be fitted between the gas regulator and the cylinder valve.)

With V_3 closed, open V_1 and V_2 and evacuate the lines down to the cylinder spindle valve, then close V_2, open the cylinder spindle valve, and adjust the regulator to give a pressure between 10 and 20 psig.

With V_L and V_6 closed, open V_4 and V_5 and evacuate the connecting pipework and condensation tube (which should be at ambient temperature at this stage), for at least 30 min. If convenient, the condensation tube should be pumped overnight, as this will ensure low background figures.

Cool the condensation tube with liquid nitrogen, then close V_4 and open V_L. (The inlet leak assembly *L*, and tube *C*, are now connected to the ion source of the mass spectrometer.)

When the peak at *m*/*e* 28 becomes constant record the instrument blank spectrum from *m*/*e* 2 to *m*/*e* 44.

Close V_5, open V_3 and V_6 (in that order) and adjust V_1 to give a flow of carbon dioxide, as indicated by Rotameter *R*, of between 0·5 and 1·0 l./min.

Allow at least 20 min for the ion beams to stabilize and then record the mass spectrum between *m*/*e* 2 and *m*/*e* 44.

Close V_1, V_3 and V_6, open V_5 and close the cylinder spindle valve.

Calculate the analytical results by reference to calibrations obtained using standards, prepared dynamically,[3] which have been previously analysed by the procedure outlined above.

When all analyses have been completed, or when the condensation tube *C* is blocked with solid carbon dioxide, close V_L, open V_4, and allow the condensation tube to reach ambient temperature whilst pumping all the solidified carbon dioxide away, then close V_4.

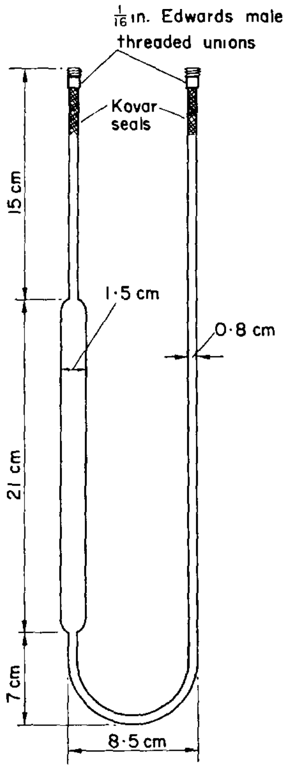

FIG. 3—Condensation tube

TABLE I.—RESPONSE TIME OF THE INLET SYSTEM AND THE MASS SPECTROMETER TO IMPURITIES AT THE 10 VPM LEVEL.

Impurity	H_2	He	CH_4	Ne	N_2	CO	O_2	Ar
Response time, *min*	2	5	12	9	7	10	9	7

RESULTS

The results, Table II, were considered satisfactory. Calibration curves obtained by using a dynamic gas-blending rig[3] were essentially linear over the range 0–30 vpm for each of the impurities. The instrument sensitivity factors for each impurity, derived from these calibration curves, are given in Table III.

It is perhaps advisable at this stage to point out that, although the apparatus used for the construction of the vacuum lock is not strictly "high-vacuum" equipment, and the instrument background is therefore higher than normal when V_L is open, the gain in sensitivity obtained by using the analysis technique described actually reduces the background/signal ratio. Typical background figures of the normal system and the modified system are shown in Table IV, together with their significance in terms of vpm of impurities in a carbon dioxide sample.

Hydrocarbon impurities

Since most hydrocarbon impurities, other than methane, would probably be sorbed on to the carbon dioxide layer (at 77°K) it was decided to carry out an experiment in which the carbon dioxide was reacted with a saturated potassium hydroxide

TABLE II.—REPEAT ANALYSES OF CARBON DIOXIDE BLENDS PREPARED IN GAS CYLINDERS AT 500 psig

Blend 1	H_2, *vpm* (*m/e* 2)	He, *vpm* (*m/e* 4)	CO, *vpm* (*m/e* 12)	CH_4 *vpm* (*m/e* 15)	Ne, *vpm* (*m/e* 20)	N_2 + CO, *vpm* (*m/e* 28)	O_2 *vpm* (*m/e* 32)	Ar, *vpm* (*m/e* 40)
Range of results from	7·75	7·80	6·94	6·49	7·24	15·58	9·33	7·93
Range of results to	8·08	8·20	7·53	6·93	8·00	16·08	9·63	8·17
Number of results	9	9	9	10	10	10	10	10
Mean	7·87	8·00	7·31	6·70	7·54	15·80	9·48	8·02
Standard deviation	0·11	0·15	0·18	0·14	0·23	0·16	0·09	0·08
Theoretical values of blend, calculated from PVT measurements	9	8	9	8	8	17	9	9
Blend 2								
Range of results from	3·45	3·43	3·00	2·87	2·65	6·97	3·90	3·26
Range of results to	3·60	3·59	3·43	3·15	2·82	7·35	4·01	3·48
Number of results	10	10	10	10	10	10	10	10
Mean	3·52	3·51	3·18	3·01	2·72	7·20	3·95	3·37
Standard deviation	0·06	0·06	0·16	0·09	0·07	0·14	0·04	0·08
Theoretical values of blend, calculated from PVT measurements	3·5	3·1	3·5	3·1	3·1	7·0	3·7	3·5
Blend 3								
Range of results from	1·09	1·09	0·95	0·96	0·87	2·43	1·34	1·05
Range of results to	1·18	1·15	1·06	1·02	0·93	2·60	1·46	1·10
Number of results	10	10	10	10	10	10	10	10
Mean	1·13	1·11	1·02	1·00	0·90	2·53	1·39	1·07
Standard deviation	0·03	0·02	0·04	0·025	0·023	0·06	0·04	0·018
Theoretical values of blend calculated from PVT measurements	1·2	1·1	1·2	1·1	1·1	2·8	1·4	1·2
Blend 4								
Range of results from	0·40	0·37	0·37	0·34	0·35	0·96	0·53	0·36
Range of results to	0·43	0·41	0·70	0·39	0·40	1·01	0·58	0·40
Number of results	10	10	10	10	10	10	10	10
Mean	0·42	0·40	0·50	0·37	0·37	0·99	0·55	0·38
Standard deviation	0·009	0·014	0·13	0·015	0·017	0·020	0·018	0·013
Theoretical values of blend calculated from PVT measurements	0·5	0·4	0·5	0·4	0·4	1·2	0·6	0·4

TABLE III.—INSTRUMENT SENSITIVITY FACTORS FOR IMPURITIES IN CARBON DIOXIDE

Impurity	H_2 (*m/e* 2)	He (*m/e* 4)	CO (*m/e* 12)	CH_4 (*m/e* 15)	Ne (*m/e* 20)	N_2 (*m/e* 28)	CO (*m/e* 28)	O_2 (*m/e* 32)	Ar (*m/e* 40)
Sensitivity* in vpm per "inch"	0·137	0·269	0·843	0·0315	0·0841	0·0166	0·0156	0·0215	0·0098

* The amplifier on the mass spectrometer has ten sensitivity ranges and all ion beam measurements are finally converted to range-seven readings for calculation of results. The conventional method of measuring ion beams is to denote a full scale deflection of ten divisions on the output meter, when on range seven, as ten "inches".

TABLE IV.—TYPICAL BACKGROUND FIGURES OF THE NORMAL AND MODIFIED SAMPLING SYSTEMS

m/e	Normal background, *in.* R7	Equivalent vpm of impurity (using normal sampling system)	Background with sorption tube *in.* R7	Equivalent vpm of impurity (using modified sampling system)
2	0·08	120 (H_2)	0·16	0·02 (H_2)
4	<0·02	<100 (He)	<0·02	<0·005 (He)
12	<0·02	—	0·25	0·21 (CO)
14	0·02	—	0·18	—
15	<0·02	<20 (CH_4)	0·02	0·0006 (CH_4)
16	0·07	—	1·00	—
17	1·00	—	7·00	—
18	4·25	—	31·50	—
19	0·01	—	0·22	—
20	<0·02	<60 (Ne)	0·05	0·004 (Ne)
22	<0·02	—	0·08	—
28	0·92	640 (N_2 + CO)	5·35	0·09 (N_2 + CO)
32	0·43	430 (O_2)	2·10	0·04 (O_2)
40	0·02	10 (Ar)	0·20	0·002 (Ar)
44	0·08	50 $(CO)_2$	9·50	—

Calculations in this table assume that the smallest ion beam height which can be detected is 0·02 inches on sensitivity range 7 (R7), and that a normal analysis is carried out using one dose of gas.

solution, and the residual gases, if any, were analysed mass-spectrometrically. The results of several tests, in which amounts ranging from 8 to 50 g of carbon dioxide sample were taken, indicated the presence of sub-vpm levels of C_2 and C_3 hydrocarbons in the residual gases.

Application of the method to the inspection of high-purity carbon dioxide

The high-vacuum low-temperature separation technique has been in use for over 12 months. It has been found that approximately six samples of carbon dioxide can be analysed before the condensation tube becomes blocked with solid carbon dioxide, but more samples could probably be handled if the dimensions of the tube were increased. This would, however, inevitably lead to an overall increase in response time of the apparatus which would tend to offset the improvement obtained due to the increased capacity of the condensation tube. Some typical analysis figures obtained for high-purity carbon dioxide are shown in Tables V and VI.

TABLE V.—TYPICAL ANALYSIS FIGURES OBTAINED FROM LIQUID CARBON DIOXIDE SAMPLES

Cyl.	H_2, *vpm*	He, *vpm*	CH_4, *vpm*	Ne, *vpm*	N_2 + CO, *vpm*	O_2, *vpm*	Ar, *vpm*
1	<0·1	<0·1	<0·1	<0·1	0·5	0·4	<0·1
2	<0·1	<0·1	<0·1	<0·1	7·6	2·0	<0·1
3	<0·1	<0·1	<0·1	<0·1	0·5	0·2	<0·1
4	<0·1	<0·1	<0·1	<0·1	11·0	2·5	0·2
5	<0·1	<0·1	<0·1	<0·1	24	4·6	0·7
6	<0·1	<0·1	<0·1	<0·1	13 12	2·9 2·6	0·3
7	<0·1	<0·1	<0·1	<0·1	13	2·5	0·3
8	<0·1	<0·1	<0·1	<0·1	0·6	0·2	<0·1
9	<0·1	<0·1	<0·1	<0·1	0·4	<0·1	0·1
10	<0·1	<0·1	<0·1	<0·1	1·4	0·4	<0·1
11	<0·1	<0·1	<0·1	<0·1	0·2	<0·1	<0·1
12	<0·1	<0·1	<0·1	<0·1	0·1	<0·1	<0·1

TABLE VI.—VARIATION IN IMPURITY CONTENT OF GAS, DURING THE LIFE OF THE CYLINDER*

Run	Date	H_2, *vpm*	N_2 + CO, *vpm*	O_2, *vpm*	Ar, *vpm*	CO_2 taken from cylinder, *l.*
1	2.9.65	<0·1	0·3	0·1	<0·1	full cylinder
2	2.9.65	<0·1	0·5	0·2	<0·1	105
3	3.9.65	<0·1	0·5	0·2	<0·1	400
4	6.9.65	<0·1	0·4	0·2	<0·1	1400
5	7.9.65	<0·1	0·3	<0·1	<0·1	1650

* These results were obtained by taking a gas phase sample of carbon dioxide

DISCUSSION

It has been successfully demonstrated that a high-vacuum, low-temperature, separation technique can be used together with a mass spectrometer (A.E.I. Model MS2.G), for the analysis of high-purity carbon dioxide. The sensitivity of the method is several orders of magnitude better than that of the normal mass spectrometric methods, and the ultimate detection limits, calculated as twice the background figures obtained from the mass spectrometer, are better than 0·01 vpm for H_2, He, CH_4, Ne, and Ar, and better than 0·2 vpm for O_2 and N_2 + CO.

Further confirmation of the utility of the method was obtained from special tests carried out on a cylinder of high-purity carbon dioxide, using both the separation technique and gas chromatography, for the determination of H_2, N_2 + CO, O_2 and Ar. The results are shown in Table VII.

TABLE VII.—RESULTS OBTAINED FROM ANALYSING A SAMPLE OF HIGH-PURITY CARBON DIOXIDE BY VARIOUS TECHNIQUES.

Method	N_2 + CO, *vpm*	O_2, *vpm*	Ar, *vpm*	H_2, *vpm*
M.S. (high vac. separation technique)	0·8	0·2	<0·1	<0·1
G.C. (silica gel column with M.S. detection)	1·2	0·2	<0·2	<0·2
G.C. (mol. sieve 5A column with helium ionization detector)	1	(O_2 + Ar < 1)		<1
G.C. (silica gel column with helium ionization detector)	total, approximately 1 vpm			

There is every indication that the sensitivity could be improved still further by either increasing the sampling rate of carbon dioxide into the condensation tube, or by reducing the instrument background. This however, assumes that no problems arise due to impurities being permanently sorbed onto the condensed carbon dioxide at these low levels. The apparatus described could be used with most types of gas-source mass spectrometer. With suitable modification (*i.e.*, two condensation tubes in parallel) the system could be arranged to work on a continuous basis and may well find applications in fields such as reactor cooling systems.

It should also be possible to use this separation technique for the analysis of high-purity nitrous oxide, even though the vapour pressure of nitrous oxide at 77°K is higher than that of carbon dioxide.

Zusammenfassung—Eine kontinuierliche Abtrennmethode bei tiefer Temperatur und Hochvakuum zusammen mit einem Massenspektrometer wurde zur Analyse von Kohlendioxid verwendet, das vpm-Mengen H_2, He, CH_4, Ne, N_2, CO, O_2 und Ar enthielt. Die Methode beruht auf der Kondensation von Kohlendioxid an den Wänden eines mit flüssigem Stickstoff gekühlten U-Rohrs aus Glas zwischen Einlaß und Ionenquelle. Eine Kohlendioxidprobe unter hohem Druck tritt also durch das Einlaßventil ein, nur die Verunreinigungen jedoch passieren das U-Rohr und erreichen die Ionenquelle: damit erzielt man eine beträchtliche Erhöhung der Empfindlichkeit und die Störung durch Kohlendioxid wird beseitigt. Die Empfindlichkeit der Methode ist um mehrere Größenordnungen besser als die der normalen massenspektrometrischen Methode.

Résumé—On a utilisé une technique de séparation en continu, sous vide élevé, à basse température, en relation avec un spectromètre de masse pour l'analyse de gaz carbonique contenant, en volume, des parties par million de H_2, He, CH_4, Ne, N_2, CO, O_2 et Ar. La méthode repose sur la condensation du gaz carbonique sur les parois d'un tube de verre en U, refroidi dans l'azote liquide, monté entre une arrivée et la source ionique. Un échantillon de gaz carbonique sous haute pression pénètre ainsi par l'orifice d'entrée mais seules les impuretés traversent le tube en U et atteignent la source ionique, avec pour conséquences un gain considérable en sensibilité et la suppression de l'interférence dûe au gaz carbonique. La sensibilité de la méthode est meilleure de plusieurs ordres de grandeur que la méthode de spectrométrie de masse normale.

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COULOMETRIC TITRATION OF ACIDS IN NON-AQUEOUS SOLVENTS

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Summary—Coulometric titrations of mineral acids, sulphonic acids, carboxylic acids, enols, imides and phenols have been carried out in t-butanol or in acetone with electrically generated tetrabutylammonium hydroxide. Either a potentiometric titration or a visual indicator end-point may be used. The amount of acid titrated ranges from 10 to 60 μequiv, and the precision and accuracy of the method are excellent.

IN RECENT years methods have been developed for the titration of acidic organic compounds in non-aqueous solvents such as pyridine,[1] acetone[2] and t-butanol.[3] A quaternary ammonium hydroxide or alkoxide titrant is better than a lithium, sodium or potassium salt because a quaternary ammonium salt formed in the titration is more likely to be soluble. In addition, an alkali metal salt may prevent the use of the glass electrode as a dependable indicator electrode in some solvents.

A disadvantage of quaternary ammonium hydroxide titrant is the difficulty of preparing it free from impurities. Carbonate and tertiary amines from the Hofmann degradation of the quaternary ammonium hydroxide are difficult to avoid. Marple and Fritz[4] showed how to remove these impurities from solutions of tetrabutylammonium hydroxide, but the process is rather long and involved.

In principle, coulometric titration of acids should avoid these difficulties. Coulometric titration is especially useful for titration of very small amounts of acids. For weak acids, a coulometric titration should be performed in a non-aqueous solvent containing very little water. Crisler and Conlon[5] titrated acids coulometrically in a benzene–methanol solution with lithium chloride as electrolyte. Johansson[6] generated bases electrolytically and successfully titrated acids in isopropanol and in a mixture of isopropanol and ethyl methyl ketone. Streuli *et al.*[7] showed that acids may be titrated coulometrically in acetone with a quaternary ammonium halide as the electrolyte for generation of the base. Williams and his students[8] generated quaternary ammonium hydroxide titrant coulometrically for the titration of acids in a benzene–methanol mixture and in t-butanol.

Although successful to a degree, the methods cited have been limited in scope. The weakest type of acid titrated successfully has been carboxylic, and the accuracy has

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been limited to approximately ±1–4%. In the present work a wide variety of acidic compounds has been titrated coulometrically in t-butanol and acetone. Substances determined include phenol and other very weak acids. The precision and accuracy for the titration of 10–60 μequiv is excellent. The end-point of the titration may be detected either by use of a visual indicator or potentiometrically.

DEVELOPMENT OF THE METHOD

The conditions for the successful titration of a weak acid in non-aqueous media may be summarized as follows. The solvent used should not have acidic properties and should be nearly anhydrous, as the presence of water causes less sharp end-points for weak acids. A quaternary ammonium hydroxide titrant, rather than an alkali metal titrant, should be used and must be essentially free from basic impurities such as carbonate and aliphatic amines. Potentiometric titrations may be performed by using a glass and a calomel electrode. For routine titrations the use of a visual indicator is advantageous.

In the coulometric titration technique developed the following system is used.

Cathode compartment. A platinum electrode of large area is used. The cathode compartment is filled with 0·1M tetrabutylammonium bromide in t-butanol. Since the t-butanol contains approximately 0·2% water (Karl Fischer titration), the probable electrode reaction is

$$H_2O + e^- \rightarrow OH^- + \tfrac{1}{2}H_2(g)$$

Anode compartment. A platinum electrode is used because difficulty was encountered with the silver halide coating that forms on a silver electrode. The compartment is filled with 0·1M tetramethylammonium bromide in methanol, which has a lower electrical resistance than t-butanol. The electrode reaction is

$$Br^- \rightarrow \tfrac{1}{2}Br_2 + e^-$$

Compartment divider. An anion-exchange membrane is used to separate the anode and cathode compartments. (In some cases a cation-exchange membrane was placed behind the anion-exchange membrane on the anode side, but this appears to be unnecessary.) The membrane used offers lower electrical resistance than does a glass frit. Also, hydrostatic pressure does not force the anode liquid through the anion-exchange membrane as it does with a glass frit.

Indicator titrations. The titration cell is a plastic box consisting of two square compartments side by side, separated by an anion-exchange membrane (Fig. 1). Each compartment contains approximately 15 ml of electrolyte solution. A suitable indicator for the titration of a particular acid is selected from the published transition ranges in t-butanol[9] after a potentiometric titration has been done to ascertain the end-point potential for the acid being titrated.

Potentiometric titrations. The titration cell used is shown in Fig. 2. The non-aqueous salt bridge to the calomel reference electrode is of a type used by Marple and Fritz[4] and gives a reproducible reference potential. A general-purpose glass indicator electrode is used. A combination glass–calomel electrode is convenient when the absolute values of the potentials are not important.

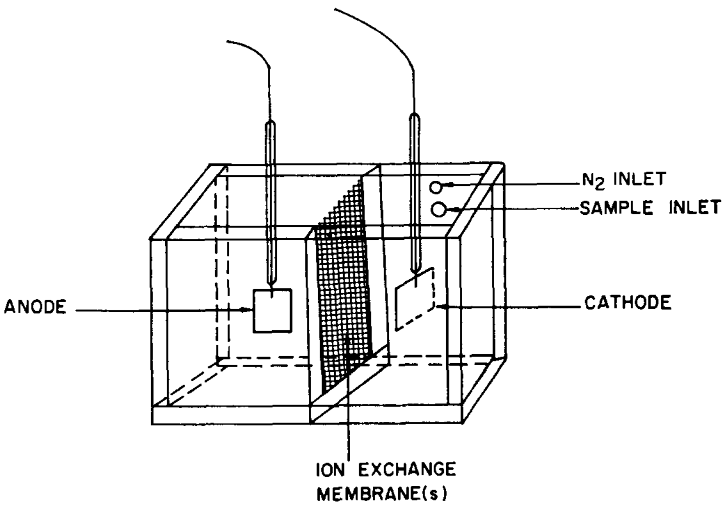

FIG. 1.—Coulometric titration assembly for indicator end-points in t-butanol.

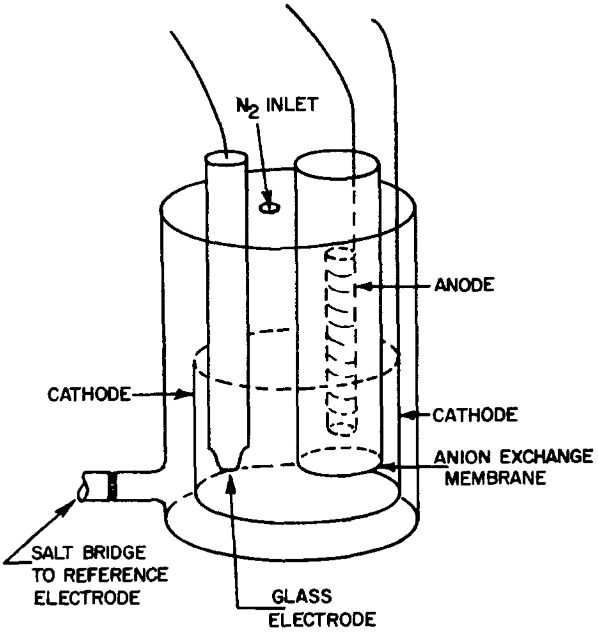

FIG. 2.—Coulometric titration assembly for potentiometric end-points in t-butanol.

EXPERIMENTAL

Apparatus

Current supply. Constant current for the generation of basic titrant was supplied by a Sargent Model IV Coulometric Current Source.

Generating electrodes. Two sheet platinum electrodes served as generating electrodes (anode and cathode) for all titrations. For potentiometric end-points the cathode was 19·3 cm^2 in area, and the anode 16·6 cm^2. Contact with the current source was made through platinum wires spot-welded to the platinum sheets. When indicator end-points were used both generating electrodes were about 4 cm^2 in size.

Measuring electrode system. Solution potentials were measured with a Corning Model 12 pH Meter and the glass–modified calomel electrode system developed by Marple and Fritz.[4]

Titration cells. The potentiometric titration cell for the generation of base is shown in Fig. 2, and is just a small scale replica of the titration cell recommended by Marple and Fritz.[4] Only half of the assembly is shown in the figure. The cathode compartment was made of glass tubing 8 cm long and 3 cm in internal diameter. The anode compartment was made of plexiglas tubing 10 cm long and 9·5 mm in internal diameter, with a disc of anion-exchange membrane fixed to one end with epoxy glue or Eastman No. 910 adhesive. The Eastman adhesive had the advantage of being readily usable and quick-drying.

Figure 1 shows the cell design that was used for coulometric titrations with indicator end-points. The cell was made of ¼-in. thick plexiglas having all sides cemented by use of ethylene dichloride. The cell consisted of two halves of a rectangular box which were clamped together by threaded rods and wing nuts. The membranes and plastic, if used, were placed between these halves, thus forming the anode and cathode compartments with internal dimensions 1 × 1 × 2 in. The cell was made leak-proof by placing rubber cement in the cracks between the two halves (sides and bottom) after clamping them together. A plexiglas cover was made and used on the box to reduce atmospheric effects on the test solutions.

Ion-exchange membranes. The cation-exchange membrane Nepton 61AZL065 and the anion-exchange membrane Nepton 111BZL065, were obtained from Ionics, Inc., Cambridge, Mass. The selective cation-exchange membrane was comprised of sulphonated co-polymers of vinyl compounds. The selective anion-exchange membrane was comprised of co-polymers of vinyl compounds containing quaternary ammonium groups and tertiary amine groups. Both types of membrane were homogeneous films cast in sheet form on a synthetic cloth backing.

Reagents

Reagent grade t-butanol was purified by fractional distillation. Reagent grade tetramethylammonium bromide and polarographic grade tetrabutylammonium bromide were used. Solutions of acid samples in t-butanol were prepared such that a 2·00 ml aliquot could be used for titration. Dilute solutions of the various indicators were prepared. A 0·1*M* solution of tetrabutylammonium bromide in t-butanol was used as the supporting electrolyte.

Procedure A (visual indicator)

Add 10–15 ml of 0·1*M* tetrabutylammonium bromide in t-butanol and several drops of the appropriate indicator to the cathode compartment. Add an equal volume of 0·1*M* tetramethylammonium bromide in methanol to the anode compartment. Set the cell cover and generating electrodes in place and bubble a slow stream of nitrogen through the cathode solution to purge it of dissolved carbon dioxide. With a slow stream of nitrogen passing over the cathode solution and with the magnetic stirrer on, generate titrant at the 0·005 setting (~5 mA), 0·01 setting or, 0·02 setting until the indicator changes colour. Then add the sample and titrate it to the same colour change using the same setting to generate the titrant base. Calculate the amount of acid present from the number of coulombs passed, after subtracting the blank.

Procedure B (potentiometric titration)

Use the titration cell shown in Fig. 2, with a glass indicator electrode and a calomel reference electrode with a salt-bridge of the type previously described.[4] If reproducible potentials are not important, a combination glass–calomel electrode may be used instead. Place in the cathode compartment approximately 10–15 ml of 0·1*M* tetrabutylammonium bromide in t-butanol and purge with nitrogen. Add approximately 5 ml of 0·1*M* tetramethylammonium bromide in methanol to the anode compartment. With a slow stream of nitrogen passing over the cell solution and with magnetic stirring, generate the base in several increments at the 0·005 setting (~5 mA). After each increment, measure and record the potential of the glass-calomel pair. Continue this process somewhat beyond the blank end point so that a blank titration curve may be constructed. Add the sample, switch to the 0·02 setting (~20 mA), and repeat the incremental generation of base until the acid is titrated and data for construction of a potentiometric titration curve are available. Determine the difference between the acid and blank titrations.

RESULTS

To test the current efficiency a large number of samples of primary standard benzoic acid were titrated in t-butanol, 2,4-dinitro di'phenylamine being used as visual indicator. Results for 20–60 μequiv samples showed a current efficiency of

100·0 ± 0·5%. Therefore, it was assumed that 100·0% current efficiency could be attained in all subsequent titrations.

Results for some 354 titrations of different acids, with visual indicators, are summarized in Table I. The precision and accuracy are extremely good, especially for 1–10 mg samples. A gas chromatogram showed that the sample of 2,4-pentanedione contained some impurities. It will be noted that the coulometric method is applicable to the titration of many types of acids including weakly acidic phenols. To obtain results of the precision and accuracy reported, attention must be paid to careful measurement of the titration blank due to impurities in the solvent and reagents.

Potentiometric titration curves for some typical weak acids are shown in Fig. 3. It was found not to be possible to record titration curves while the titrant is being generated, so titration curves have to be plotted manually by generating an increment of titrant and then shutting off the coulometer while the potential is measured. In Fig. 4 curves for the titration of toluenesulphonic and benzoic acids are shown, and in Fig. 5 titration curves for some diprotic acids are illustrated. Results for quantitative potentiometric titrations in t-butanol are given in Table II.

For the accurate titration of strong acids such as those in Fig. 5, it is necessary to use very pure tetrabutylammonium bromide, to purify the solvent used and to subtract the blank which remains despite these precautions. The curves in Fig. 6 show that the solvent blank may be reduced appreciably by double distillation of the t-butanol. Purification also largely avoids the buffering effect of weak acid impurities on the titration of strong acids such as sulphuric or aromatic sulphonic acids.

The coulometric method outlined above gives excellent results for the titration of a variety of acidic compounds either potentiometrically or with visual indicators. The titrant generated electrically is of excellent purity, and the tedious preparation of pure quaternary ammonium hydroxide titrant by chemical means is obviated. However, a limitation of the coulometric method is that low current densities must be employed. With the titration cells described, the maximum current for precise results is approximately 20 mA. With a current much higher, the cell resistance increases and the current efficiency is lowered. The crux of the problem seems to be the difficulty in transporting ions at a sufficiently fast rate through an ion-exchange membrane or glass frit.

COULOMETRIC TITRATIONS IN ACETONE

Apparatus

The cell for potentiometric titrations in acetone solution differed somewhat from the cell already described. The glass cathode compartment was 8 cm high and 3 cm in internal diameter, and the anode compartment was a piece of glass tubing 10 cm long and 10·5 mm in internal diameter with an ultrafine-porosity glass fritted disc on one end. The measuring electrode system was a slender-bodied combination glass–calomel electrode with the aqueous saturated potassium chloride solution replaced by a saturated solution of potassium chloride in methanol. The generating electrode system remained the same.

Reagents

A spectrographic grade of acetone was obtained from Eastman Organic Chemicals and used in this study without further drying or purification. The acetone contained 0·35% water (v/v). The electrolyte solution for the cathode compartment was 0·1*M* polarographic grade tetrabutylammonium bromide in spectrographic grade acetone. Tetramethylammonium bromide in methanol served as electrolyte solution in the anode compartment.

Procedure

As previously described for potentiometric titrations in t-butanol.

TABLE I.—COULOMETRIC TITRATIONS IN t-BUTANOL

Compound titrated	No. of samples	Amount taken, *μequiv*	Recovery, %	Std. deviation, %	Indicator
Benzoic acid	59	10–60	$100{\cdot}1_5$	0·17	2,4-dinitroaniline
Phenol	96	12–61	100·1	0·21	2-nitroaniline
2,4,6-Trimethylphenol	7	20	$99{\cdot}7_5$	0·41	2-nitroaniline
2-Hydroxyphenol	6	20	99·4	0·19	Azo Violet
Anthranilic acid	41	10–60	100·1	0·13	2,4-dinitroaniline
Succinic acid (1st H)	13	10–20	99·7	0·08	Bromothymol Blue
(2nd H)	17	10–60	99·4	0·13	Azo Violet
Acetoacetanilide	10	20	$99{\cdot}8_5$	0·12	Azo Violet
Dibenzoylmethane	22	20–48	99·9	0·11	Azo Violet
Succinimide	25	10–60	99·9	0·22	Azo Violet
Hydantoin	16	20	99·5	0·11	Azo Violet
2-Cyanoacetamide	12	20	99·7	0·15	*p*-nitro-*p'*-aminoazobenzene
Ethyl cyanoacetate	10	20	99·1	0·07	Azo Violet
2,4-Pentanedione	8	30	97·5	0·06	Azo Violet
p-Toluenesulphonic acid	12	20–60	99·9	0·08	Bromothymol Blue

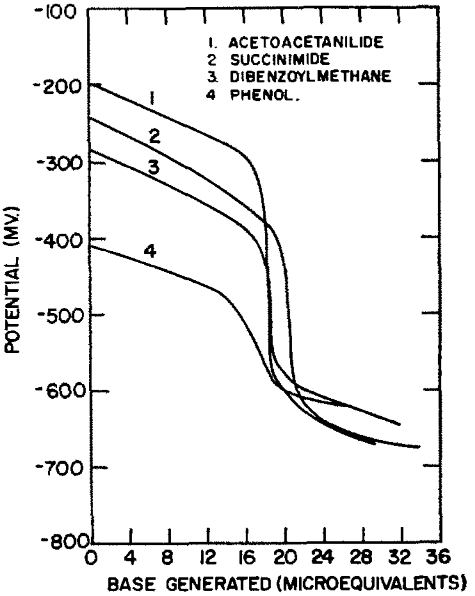

FIG. 3.—Titration of enols, imides, and phenols in t-butanol with electrolytically generated titrant.

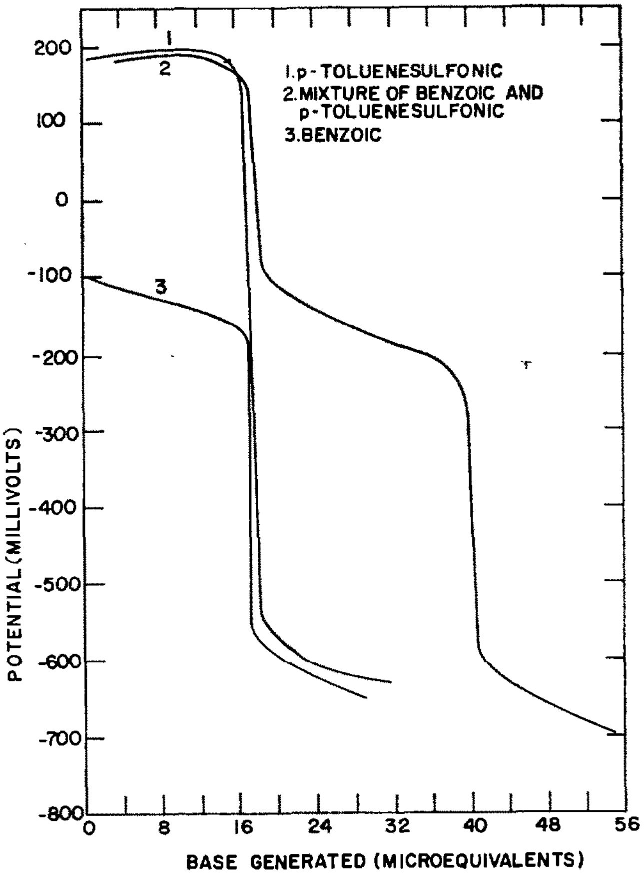

FIG. 4.—Differentiating titration of benzoic acid and *p*-toluenesulphonic acid in t-butanol with electrolytically generated titrant.

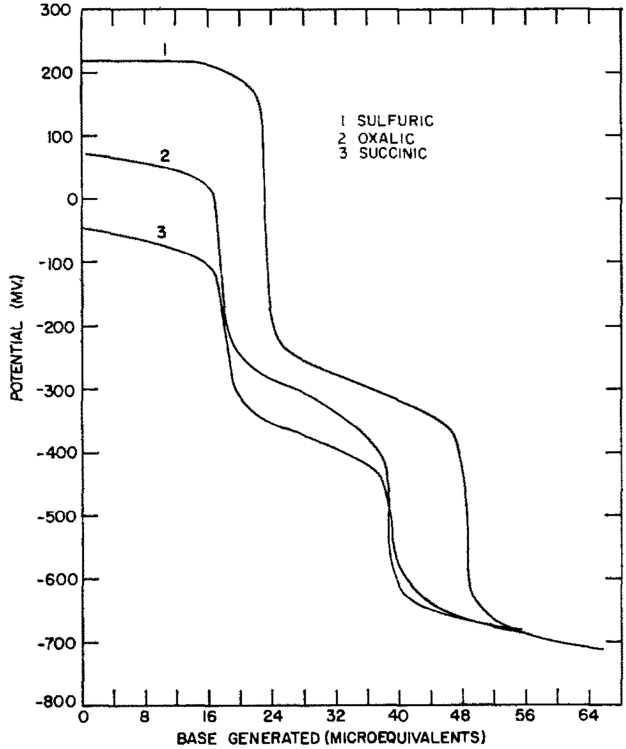

Fig. 5.—Titration of dibasic acids in t-butanol with electrolytically generated titrant.

Results

Because acetone has a much higher dielectric constant than t-butanol, the electrical resistance of solutes in acetone is much lower. This makes it possible to use a glass frit, rather than an anion-exchange membrane, to separate the anode and cathode compartments. (Also, acetone tends to dissolve the binder in ion-exchange membranes.)

Table II.—Coulometric titrations of acids in t-butanol with potentiometric end-points

Compound titrated	No. of samples	Taken, *μequiv*	Found, *μequiv*	Recovery, %
Benzoic acid	5	20·21	20·24	100·1
Phenol	4	20·08	20·26	100·9
Acetoacetanilide	2	20·03	20·14	100·5
Dibenzoylmethane	3	20·02	20·34	101·6
p-Toluenesulphonic acid	6	20·11	20·07	99·8
Sulphuric acid (1st end-point)	3	20·70	20·70	100·0
Sulphuric acid (2nd end-point)	2	50·18	50·21	100·1
Oxalic acid (1st end-point)	2	19·25	19·20	99·7
Oxalic acid (2nd end-point)	2	40·09	40·03	99·9

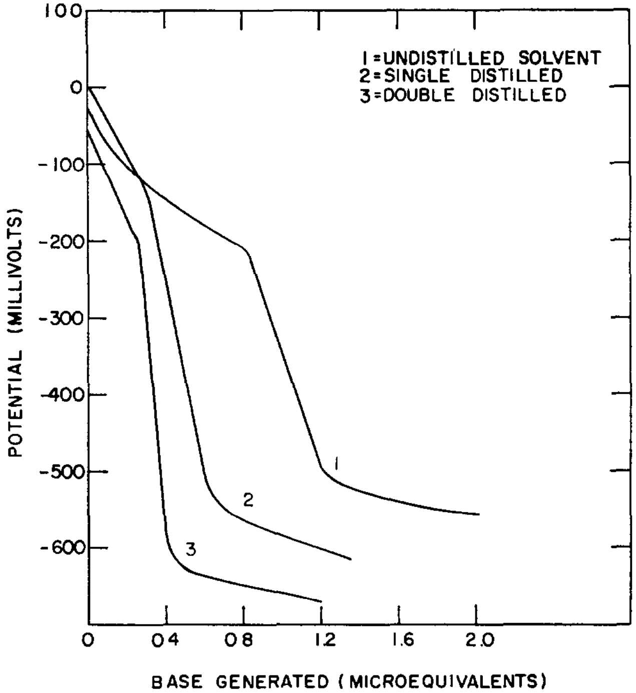

FIG. 6.—Titration of t-butanol solvent blanks with electrolytically generated titrant.

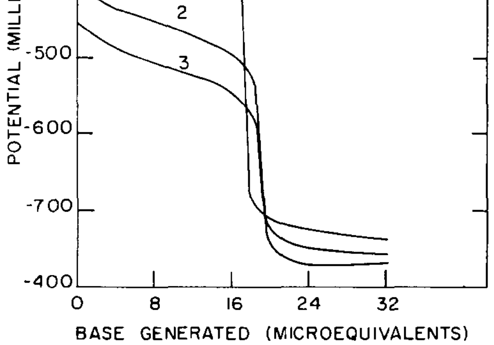

FIG. 7.—Titration of enols in acetone with electrolytically generated titrant.

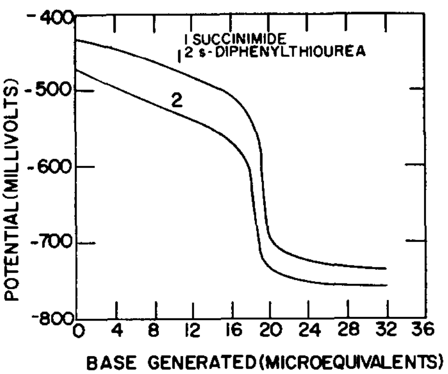

FIG. 8.—Titration of imides in acetone with electrolytically generated titrant.

TABLE III.—COULOMETRIC TITRATIONS OF ACIDS, WITH POTENTIOMETRIC END-POINTS

Compound titrated	No. of samples	Taken, *μequiv*	Found, *μequiv*	Recovery, %
Benzoic acid	3	10·06	10·16	101·0
Benzoic acid	3	20·11	20·08	99·9
Benzoic acid	3	30·17	30·94	102·6
Benzoic acid	4	60·89	60·81	99·9
Acetoacetanilide	3	10·11	10·08	99·7
Acetoacetanilide	3	20·21	20·32	100·5
Acetoacetanilide	4	30·32	30·36	100·1
Acetoacetanilide	5	40·42	40·28	99·7
Acetoacetanilide	3	60·16	59·81	99·4
5,5-Dimethyl-1,3-cyclohexanedione	4	20·16	19·55	97·0
Dibenzoylmethane	3	20·07	20·17	100·5
Succinimide	2	20·26	20·53	101·3
Phenol	1	21·13	21·15	100·1
2,4-Dinitrophenol	2	20·20	20·20	100·0
S-Diphenylthiourea	2	20·11	20·13	100·1
p-Toluenesulphonic acid	3	10·37	10·34	99·7
p-Toluenesulphonic acid	3	20·73	20·76	100·1
p-Toluenesulphonic acid	3	31·10	31·39	100·9
p-Toluenesulphonic acid	3	60·66	60·59	99·9

Electrolyte: 0·1*M* tetrabutylammonium bromide in acetone.

Titration curves for some weak acids in acetone are shown in Figs. 7 and 8. Results for quantitative coulometric titrations in acetone are given in Table III. It may be concluded that coulometric titrations in acetone by the system proposed are quite successful. However, t-butanol seems better suited to the titration of mixtures of acids, and gives a lower solvent blank than acetone does.

Zusammenfassung—Mineralsäuren, Sulfonsäuren, Carbonsäuren, Enole, Imide und Phenole wurden in t-Butanol oder Aceton mit elektrisch erzeugtem Tetrabutylammoniumhydroxid coulometrisch titriert. Man kann den Endpunkt potentiometrisch oder visuell mit einem Indikator bestimmen. Die titrierte Säuremenge reicht von 10 bis 60 μäq, Genauigkeit und Richtigkeit der Methode sind ausgezeichnet.

Résumé—On a mené des titrages coulométriques d'acides minéraux, acides sulfoniques, acides carboxyliques, énols, imides et phénols en *t*-butanol ou en acétone au moyen d'hydroxyde de tétrabutylammonium produit électriquement. On peut utiliser soit un titrage potentiométrique, soit un indicateur visuel pour le point de fin de dosage. La quantité d'acide titrée se situe entre 10 et 60 μ équiv., et la précision et la justesse de la méthode sont excellentes.

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COMPLEXATION OF URANIUM BY 2-(2-THIAZOLYLAZO)-4-METHOXYPHENOL AND 2-(2-THIAZOLYLAZO)-5-METHOXYPHENOL

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Summary—A comparative study has been made of the complexation of uranium(VI) by 2-(2-thiazolyl)-4-methoxyphenol (TAMH) and 2-(2-thiazolylazo)-5-methoxyphenol (TAMR). The complexes are less stable and have lower molar absorptivities than the PAR and TAR complexes but are still useful for determination of uranium. The TAMH chelate can be extracted into isobutyl methyl ketone. Both complexes are 1:1 metal:ligand. For the TAMH complex $\log \beta_1 = 8{\cdot}8$, $\varepsilon = 1{\cdot}4 \times 10^4$ at 610 mμ; for the TAMR complex $\log \beta_1 = 8{\cdot}1$, $\varepsilon = 2{\cdot}0 \times 10^4$ at 530 mμ.

THE *o*-substituted *N*-heterocyclic azo dyes are highly sensitive reagents for uranium and fairly suitable for its detection and spectrophotometric determination, as was shown earlier for 1-(2-pyridylazo)-2-naphthol (PAN),[1–9] 4-(2-pyridylazo)resorcinol (PAR),[10–14] 7-(2-pyridylazo)-8-hydroxyquinoline,[15] 4-(2-thiazolylazo)resorcinol (TAR)[16,17] and 2-(2-thiazolylazo)-5-dimethylaminophenol,[18,19] 2-(2-thiazolylazo)-5-diethylaminophenol.[26] On the other hand the tendency of uranium to form only 1:1 complexes, observed for PAR and TAR in aqueous solution, is of particular interest and proves the strictly terdentate function of these azo dyes in reaction with uranyl ions, as well as the tendency of the uranyl ion in solution to keep the co-ordination number four.

2-(2-Thiazolylazo)-5-methoxyphenol (TAMR) and 2-(2-thiazolylazo)-4-methoxyphenol (TAMH) have been shown to be suitable metal indicators for a number of ions,[20] and have the advantages of a simpler dissociation scheme and a large colour contrast between the reagent and the metal chelates. In this paper the reaction of uranyl ion with TAMR and TAHM is therefore described. In spite of the lower molar absorptivity and stability of their uranyl chelates, compared with those of PAR or TAR, these reagents are suitable for the spectrophotometric determination of uranium in slightly acid aqueous ethanol. The uranyl–TAMH chelate can be extracted into isobutyl methyl ketone from almost neutral aqueous nitrate solutions. Unfortunately the well-proved mixture[12] of 5-sulphosalicylic acid, fluoride and CDTA to screen interfering metal ions cannot be used and uranium has firstly to be separated.

EXPERIMENTAL

Reagents

Uranyl nitrate stock solutions in 1*M* perchloric acid or 0·5*M* nitric acid were standardized by titration with dichromate or gravimetrically with oxine.

2-(2-Thiazolylazo)-5-methoxyphenol (TAMR) and 2-(2-thiazolylazo)-4-methoxyphenol (TAMH)

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(Institute of Pure Chemicals, Lachema, Brno) were checked for purity by dichromate titration, elemental analysis and descending paper chromatography.[20] TAMR usually contains small amounts of TAR. The dyes were first dissolved in 1–2 ml of dimethylformamide (DMF) and the solutions diluted with water so that the DMF contents were not larger than 1% v/v. Solutions in dimethylformamide and 96% ethanol were also used.

Constant ionic strength $\mu = 0{\cdot}1$ was maintained during studies of equilibria, by addition of sodium perchlorate or potassium nitrate. Cetylpyridinium bromide ($10^{-2}M$) was used only in the absence of perchlorate ions. Polyvinyl alcohol, 12% acetylated, was used in fresh 1% w/v solutions filtered through a black-band paper; no Tyndall effect was observed if the solution was diluted to 0·4% w/v. The pH was adjusted with dilute ammonia or perchloric or nitric acids and measured on a Radiometer pH meter (PHM 3k) to 0·02 pH unit. The pH values for 30% v/v ethanol or dimethylformamide media were not corrected.

Buffers, used only for the determination of uranium, were: 1*M* pyridinium nitrate—81·3 ml of redistilled pyridine mixed with 46 or 30 ml of concentrated nitric acid and diluted to 1 l. (pH 4·94 or 5·36 in water); 1*M* acetate–acetic acid—136 g of sodium acetate and 60 ml of glacial acetic acid were dissolved and diluted to 2 l. (pH 4·62 in water); 0·5*M* tris(hydroxymethyl)aminomethane–nitric acid—15·14 g of "tris" and 116·5 ml of 1*M* nitric acid diluted to 250 ml (pH 6·95).

Methods

Graphical and numerical interpretations of pH-absorbance curves for various conditions were carried out,[13,15,20–23] and the method of continuous variation[24] and Asmus's in two-phase system method[25] were also used.

RESULTS

Acid-base equilibria of TAMH and TAMR

The K_{a2}-values for the proton of the hydroxy group *ortho* to the azo group were calculated from absorbance-pH plots for aqueous and 30% v/v ethanolic media by means of $C_R/A = f[H]$ transformations, logarithmic plots,[20] or the inflexion points of well-defined symmetric pH plots (C_R = analytical concentration of reagent; A = absorbance).

For TAMH (510–560 mμ), pK_{a2} was 8·12 ± 0·05 (7 values) in water ($\mu = 0{\cdot}1$) and 8·45 in 30% v/v ethanol ($\mu = 0{\cdot}1$).

For TAMR, pK_{a2} was 7·08 ± 0·04 (9 values) in water ($\mu = 0{\cdot}1$); 410–500 mμ) and 7·63 ± 0·03 (3 values) in 30% v/v ethanol ($\mu = 0{\cdot}1$; 500–530 mμ).

The value of pK_{a2} for TAMR differs from the earlier value (6·70) found in 0·5% v/v methanol,[20] because of the presence of small amounts of TAR in the earlier sample.

Absorption curves of the uranyl complexes of TAMH and TAMR

An absorbance maximum at 610–615 mμ was found for TAMH solutions containing various excesses of uranyl ion, in the pH range 2·2–3·5 (Fig. 1). The two maxima for TAMH (at 370 and 460 mμ) change to a broad inflexion at 390–420 mμ and there is an isosbestic point at 515 mμ; the ligand absorption maximum at 370 mμ is largely retained, however. The large colour contrast between the reagent and the chelate is evident, a new maximum appearing at about 610 mμ for the chelate. This maximum does not shift when equimolar solutions or excesses of reagent are used at pH $\leqslant$ 4, even in 30% v/v ethanol. At pH 5·0, with solutions containing 30% v/v ethanol and various ratios of metal ion and ligand, $\lambda_{\max}$ is 617–625 mμ and a new peak appears at about 650 mμ (Fig. 2). The nearly isosbestic point at 521 mμ proves that there is a simple complexation equilibrium and that only one complex is formed with TAMH under the various conditions. Partial hydrolysis of the complex at this pH influenced the curves when metal ion was present in excess.

The chelate extracted into isobutyl methyl ketone from solutions containing

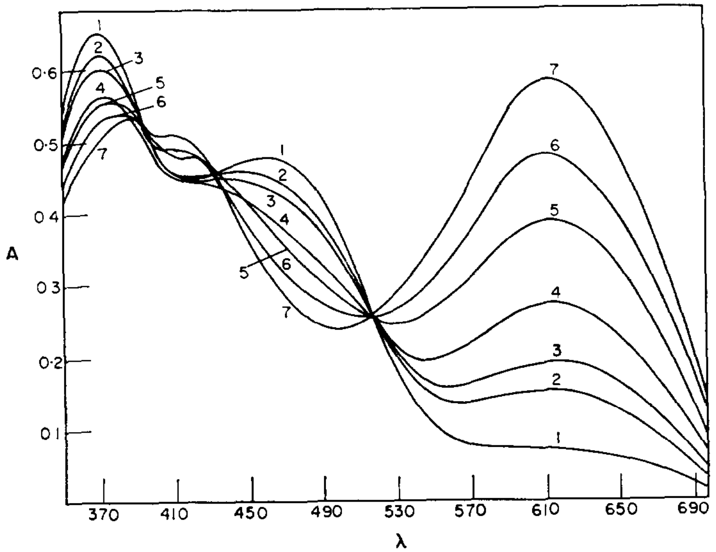

FIG. 1.—Absorption curves for TAMH solutions containing UO_2^{2+} excess. $C_M = 10^{-3}M$; $C_R = 5 \times 10^{-5}M$; pH: *1*—2·17; *2*—2·52; *3*—2·64; *4*—2·86; *5*—3·08; *6*—3·28; *7*—3·50.

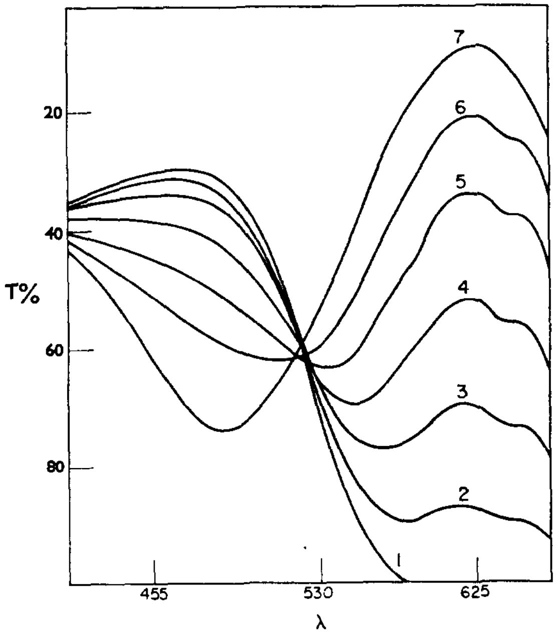

FIG. 2.—Transmittance curves for TAMH solutions containing various UO_2^{2+} concentrations at pH 5·02 in 30% v/v ethanol.
$C_R = 1{\cdot}33 \times 10^{-4}M$; CPB $= 10^{-3}M$; 0·5-cm cell.
C_M: *1*—0; *2*—$1{\cdot}33 \times 10^{-5}M$; *3*—$2{\cdot}67 \times 10^{-5}M$; *4*—$5{\cdot}33 \times 10^{-5}M$; *5*—$9{\cdot}34 \times 10^{-5}M$; *6*—$1{\cdot}33 \times 10^{-4}M$; *7*—$2{\cdot}67 \times 10^{-4}M$.

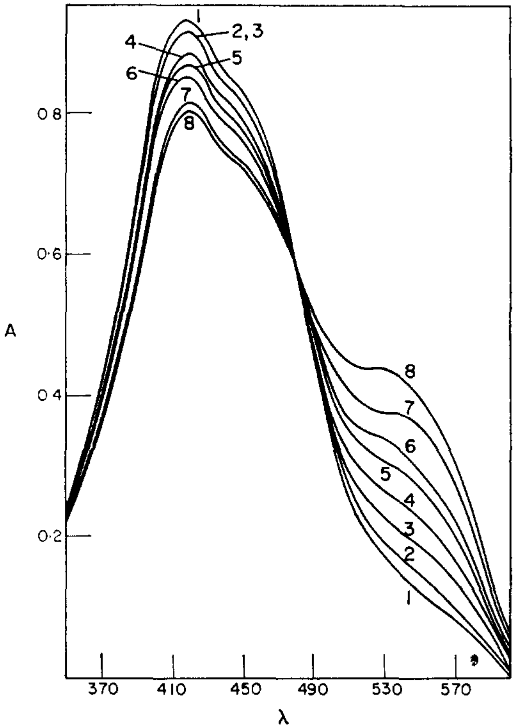

FIG. 3.—Absorption curves for TAMR solutions containing UO_2^{2+} excess. $C_M = 10^{-3}M$; $C_R = 5 \times 10^{-3}M$; pH: *1*—2·20; *2*—2·33; *3*—2·47; *4*—2·63; *5*—2·79; *6*—2·92; *7*—3·26; *8*—3·52.

nitrate and ligand excess ($C_R/C_M = 18$) has a broad absorption maximum at 600 mμ. Isoamyl alcohol solutions of the chelate (extracted from solutions with metal ion excess) retain the ligand maximum at 390 mμ but the chelate maximum is at 620 mμ for pH < 4·6.

The TAMR chelate has λ_{max} 530 mμ *in solutions containing metal ion excess*, but the ligand maximum has considerable intensity even at pH > 3·5 (Fig. 3). The maximum remains at 540 mμ for solutions with 30% v/v ethanol or dimethylformamide in the presence of a 10-fold ligand excess. The formation of only one uranyl chelate with TAMR is indicated at pH 5·0 for varied metal ion concentration in 30% v/v ethanol (Fig. 4). The maximum and isosbestic point stay at 537–540 and 480 mμ respectively. Cetylpyridinium bromide has only negligible effect on the absorption maximum at higher pH values and in the presence of ligand excess.

Absorbance-pH plots

The complexation of uranyl ion with TAMH occurs from pH 1·5 in 30% v/v ethanol solutions containing metal ion excess, becoming maximal at pH > 4, but some chelate hydrolysis was observed for equimolar solutions above this pH (Fig. 5).

The pH-absorbance plots were analysed by means of the transformations deduced and discussed earlier,[21–23] which are rather simple if a 1:1 complex is formed.

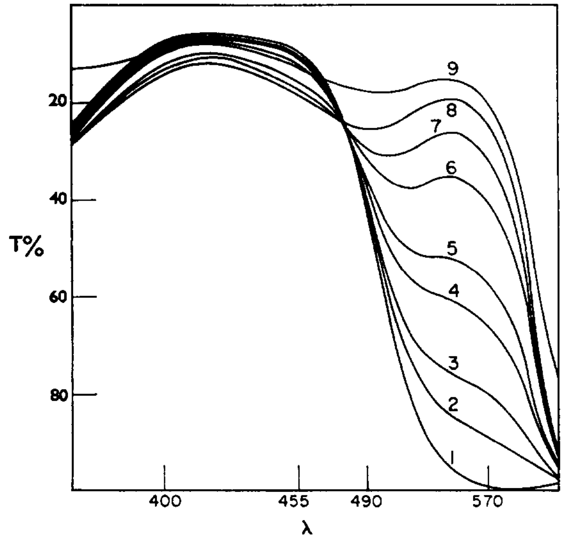

FIG. 4.—Transmittance curves for TAMR solutions containing various UO_2^{2+} concentrations at pH 4·92 in 30% v/v ethanol.
$C_R = 6{\cdot}00 \times 10^{-5} M$; CPB = $10^{-3} M$.
C_M: *1*—0; *2*—$3{\cdot}0 \times 10^{-6} M$; *3*—$6{\cdot}0 \times 10^{-6} M$; *4*—$1{\cdot}2 \times 10^{-5} M$; *5*—$2{\cdot}0 \times 10^{-5} M$; *6*—$6{\cdot}0 \times 10^{-5} M$; *7*—$1{\cdot}2 \times 10^{-4} M$; *8*—$2{\cdot}4 \times 10^{-4} M$; *9*—$6{\cdot}0 \times 10^{-4} M$.

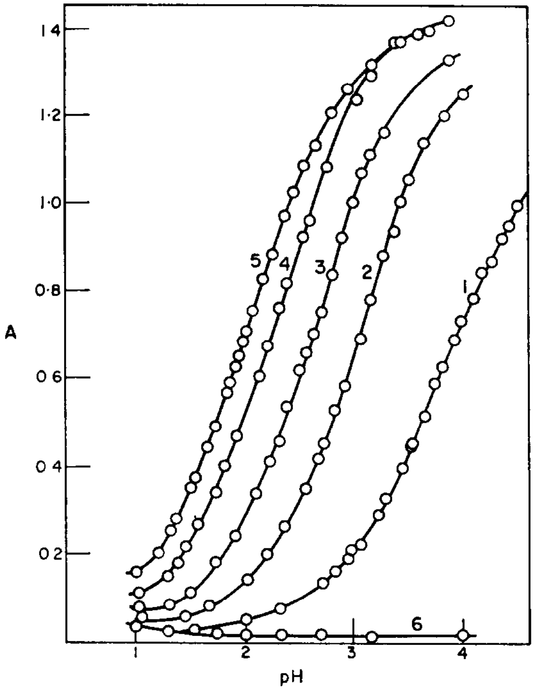

FIG. 5.—pH-Absorbance plots for TAMH solutions with various UO_2^{2+} concentrations.
$C_R = 9{\cdot}95 \times 10^{-5} M$; 30% v/v ethanol; $\lambda = 610$ mμ; $\mu = 0{\cdot}1$.
C_M: *1*—$9{\cdot}84 \times 10^{-5} M$; *2*—$3{\cdot}98 \times 10^{-4} M$; *3*—$9{\cdot}94 \times 10^{-4} M$; *4*—$2{\cdot}49 \times 10^{-3} M$; *5*—$4{\cdot}97 \times 10^{-3} M$; *6*—0.

For solutions containing excess of metal ion:

$$\frac{C_R}{A} = \frac{1}{\varepsilon_1} + \frac{[H]^x}{C_M k_1 \varepsilon_1} \tag{1}$$

$$A = \varepsilon_1 C_R - \frac{[H]^x A}{C_M k_1 \varepsilon_1} \tag{2}$$

$$\log \frac{A}{\varepsilon_1 C_R - A} = x\,\mathrm{pH} + \log C_M + \log k_1 \tag{3}$$

where ε_1 and k_1 are the molar absorptivity and the stability constant of the complex.

For equimolar solutions:

$$\frac{C_R}{A} = \frac{1}{\varepsilon_1} + \frac{1}{\sqrt{k_1 \varepsilon_1}} \sqrt{\frac{[H]^x}{A}} \tag{4}$$

$$\log \frac{A}{(\varepsilon_1 C_R - A)^2} = x\,\mathrm{pH} + \log k_1 - \log \varepsilon_1. \tag{5}$$

The absorbance of the dye can be neglected at the concentrations used, and so can the protonation of the ligand at pH $< 2{\cdot}8$ ($\mathrm{p}K_{a1} = -0{\cdot}03$).

The straight-line plots obtained for transformations (1), (2) (Fig. 6) and (4) for $x = 1$ prove there is the simple equilibrium

$$UO_2^{2+} + HR \rightleftharpoons UO_2R^+ + H^+ \tag{A}$$

The molar absorptivity values ε_1 or $A_{01} = \varepsilon_1 C_R$ calculated from the intercepts on the ordinate were substituted in the related logarithmic plots (3) and (5) which confirm the number of protons liberated during complexation and were used for the calculation of stability constants. According to (1), (2) and (4) ε_1 is $(1{\cdot}3\text{–}1{\cdot}4) \times 10^4$ for the TAMH-UO_2 chelate at 610 mμ.

The analogous TAMR chelate is formed above pH 2 and the pH-absorbance plots (Fig. 7) were partly influenced by the protonation of the ligand ($\mathrm{p}K_{a1} = 0{\cdot}98$) at pH 2·5, and by partial hydrolysis of the chelate at pH $\geqslant$ 4.

The necessary transformations are as follows, if two light-absorbing forms of the ligand, H_2R^+ and HR, are simultaneously present and only HR reacts to form the 1:1 chelate.

For excess of metal ion in solution:

$$\frac{C_R}{A} = \frac{1}{\varepsilon_1} + \frac{(A - \varepsilon_R C_R)[H]^x}{A C_M k_1 \varepsilon_1} \tag{6}$$

$$\frac{C_R}{A} = \frac{1}{\varepsilon_1} + \frac{\{A(1 + [H]/K_{a1}) - \bar{\varepsilon}_R C_R\}[H]^x}{A C_M k_1 \varepsilon_1} \tag{7}$$

$$A = \varepsilon_1 C_R - \frac{\{A(1 + [H]/K_{a1}) - \bar{\varepsilon}_R C_R\}[H]^x}{C_M k_1 \varepsilon_1} \tag{8}$$

$$\log \frac{(1 + [H]/K_{a1}) - \bar{\varepsilon}_R C_R}{\varepsilon_1 C_R - A} = x\,\mathrm{pH} + \log C_M + \log k_1 \tag{9}$$

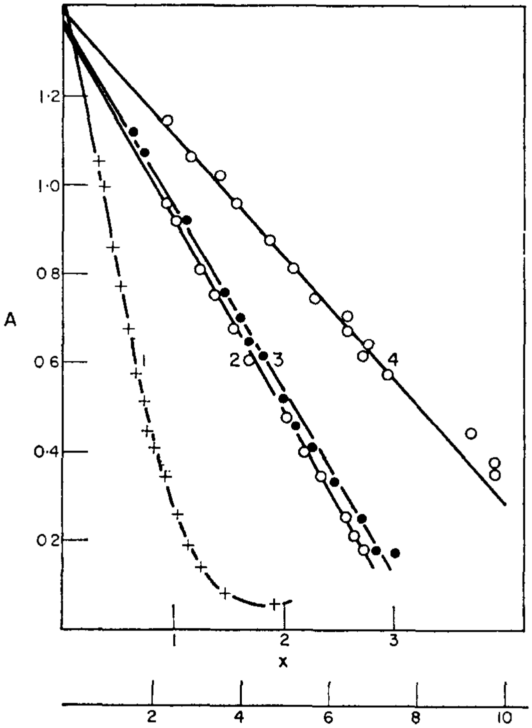

FIG. 6.—Graphical analysis of pH-absorbance plots, by equation (2), for TAMH system.
$C_R = 9{\cdot}95 \times 10^{-5}M$; C_M/C_R: *1*—4; *2*—10; *3*—25; *4*—50; $x = A[\mathrm{H}] \times 10^3$.

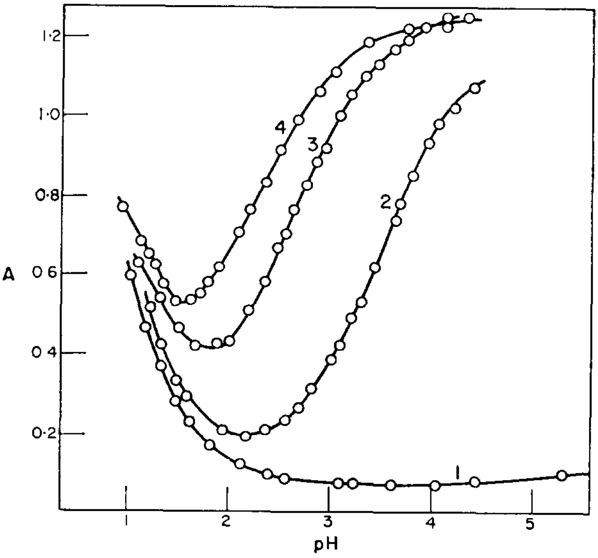

FIG. 7.—pH-Absorbance plots for TAMR solutions with various UO_2^{2+} concentrations, at 530 mμ ($\mu = 0{\cdot}1$, 30% v/v ethanol).
$C_R = 9{\cdot}95 \times 10^{-5}M$; C_M: *1*—0; *2*—$9{\cdot}95 \times 10^{-5}M$; *3*—$9{\cdot}94 \times 10^{-4}M$; *4*—$2{\cdot}49 \times 10^{-3}M$.

where $\bar{\varepsilon}_R = \varepsilon_{R1}[H]/K_{a1} + \varepsilon_{R2}$ and ε_{R1} and ε_{R2} are the molar absorptivities of the reagent species.

For equimolar solutions and only HR considered,

$$\frac{C_R}{A} = \frac{1}{\varepsilon_1} + \frac{\sqrt{[H]^x(A - \varepsilon_R C_R)}}{A\varepsilon_1}\sqrt{\frac{\varepsilon_1 - \varepsilon_R}{k_1}} \tag{10}$$

$$\log \frac{A - \varepsilon_R C_R}{(\varepsilon_1 C_R - A)^2} = x\,\text{pH} + \log k_1 - \log(\varepsilon_1 - \varepsilon_R). \tag{11}$$

$\varepsilon_R C_R$ and $\bar{\varepsilon}_R C_R$ are read directly from the pH-absorbance curves for the reagent alone, at the same concentration.

For the TAMR chelate the molar absorptivities ε_1 or $A_0 = \varepsilon_1 C_R$ calculated from the intercepts of the graphical plots of (6), (7) and (8) are smaller for $\lambda = 530$ mμ than those calculated for solutions with ligand excess, *i.e.*, $\varepsilon_1 = (1{\cdot}3\text{–}1{\cdot}4) \times 10^4$. This does not arise from a further uranyl chelate with TAMR but rather from the partial hydrolysis of the chelate in solutions containing metal ion in excess.

The equilibrium (A) is again proved (one proton liberated during complexation). However, the divergence of points in the acid region (*cf.* Fig. 8), which is smaller if the absorbance term is not corrected for the protonated reagent [equation (6)], is rather evidence that both forms of the reagent, *i.e.*, HR and H_2R^+, react simultaneously and the equilibrium (B) is also valid:

$$UO_2^{2+} + H_2R^+ \rightleftharpoons UO_2R^+ + 2H^+ \tag{B}$$

Continuous variations

A maximum for a 1:1 ratio of M:R results on the Job curves for solutions of TAMR with $C_{total} = 1{\cdot}0 \times 10^{-5}M$ at pH 5·9 (borate buffer) and 530–550 mμ, and for the TAMH chelate at pH 6·95 (borate buffer) and 620–640 mμ. This is also true for solutions containing 40% v/v dimethylformamide The borate buffer is without influence on the position of the maximum. The same results were obtained for the TAMH chelate at pH 4·95 (pyridine buffer) in 30% v/v ethanol.

Equilibrium and stability constants

Equilibrium constants were calculated from graphical logarithmic plots, (3) and (5), for zero value of the left-hand side:

$$\log k_1 = -\log C_M - \text{pH} \tag{12}$$

$$\log k_1 = -\text{pH} + \log(\varepsilon_1 - \varepsilon_R) \tag{13}$$

The stability constant K_1 is obtained from $K_1 = k_1/K_{a2}$, where $k_1 = [MR][H]/[M][HR]$ and $K_1 = [MR]/[M][R]$.

Table I.—Constants for uranyl-chelates

	TAMH	TAMR
$\log k_1$	0·4* 0·3† 0·4†	0·5* $0{\cdot}4_4$† 0·4†
$\log K_1$	$8{\cdot}8_5$ $8{\cdot}7_5$	$8{\cdot}1_5$ $8{\cdot}0_5$

* Equation (13).
† Equation (12).
Valid for $\mu = 0{\cdot}1$ and 30% v/v ethanol.

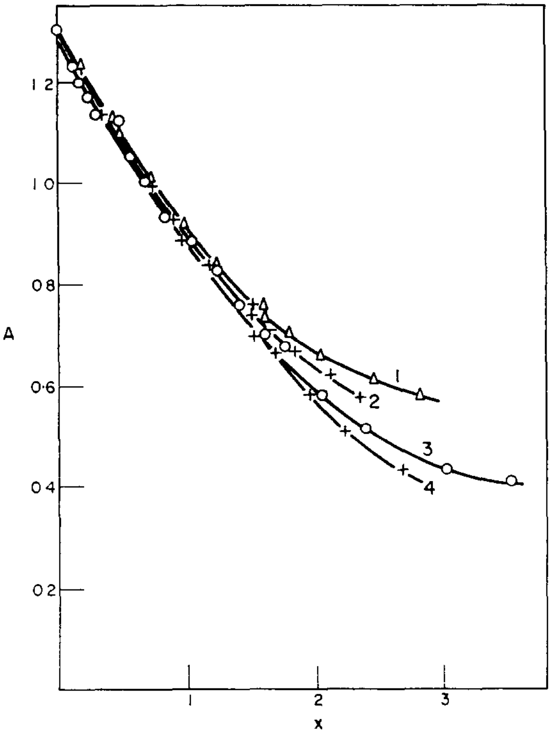

FIG. 8.—Graphical analysis of TAMR system pH-absorbance plots, by equation (8). $C_R = 9{\cdot}95 \times 10^{-5}M$; C_M/C_R: *1*—25 [$x = (A\alpha - A_{0R})[\mathrm{H}] \times 10^8$]; *2*—25 [$x = (A - A_{0R})[\mathrm{H}] \times 10^8$]; *3*—10 [$x = (A\alpha - A_{0R})[\mathrm{H}] \times 10^8$]; *4*—10 [$x = (A - A_{0R})[\mathrm{H}] \times 10^8$]. $\alpha = 1 + [\mathrm{H}]/K_{a1}$

DETERMINATION OF URANIUM WITH TAMR

Although the uranium-TAMR chelate is formed over a broad pH range, it and the ligand partially precipitate even from solutions as dilute as $2 \times 10^{-5}M$, but especially if an excess of reagent is present and the pH is >4, and the chelate and ligand are adsorbed on glass or polyethylene surfaces. Hence a 30% v/v ethanol medium was used and a protective colloid added. Gelatine was without effect but polyvinyl alcohol (0·2% w/v) and cetylpyridinium bromide ($10^{-3}M$) were suitable at pH 5·2–5·4 and did not appear to interact with the reagent at pH <7. The absorbance is maximal at pH 5·0–5·2, $\lambda = 530$ mμ, $\mu \rightarrow 0$, for solutions with $C_R/C_M > 8$, or at pH 4·5–5·0 if cetylpyridinium bromide is used. The reagent itself absorbs strongly for pH <2·5 or >5·5 as a result of protonation and dissociation respectively.

The colour is fully developed in 5–10 min, at pH 4·5–5·2, and is stable for at least 6 hr. At pH 5·6 maximum absorbance at 530–560 mμ was reached if the reagent excess was 5-fold and 20–30% v/v ethanol and 0·2 w/v polyvinyl alcohol were present, but at least an 8-fold excess of reagent was used for determinations.

Acetate, even at $10^{-2}M$ concentration, considerably decreases the absorbance of the solutions at pH 4–5, but pyridine buffers to 0.1M (pH 4·6–5·0) do not. With 0·1M pyridine buffer, pH 4·8–5·0, the maximal absorbance at 530–550 mμ was reached in the presence of 10-fold reagent excess and $5 \times 10^{-4}M$ cetylpyridinium bromide if the solutions contained either ethanol or dimethylformamide in 30% v/v concentration.

Beer's law is obeyed for 0·5–9·5 ppm of uranium, at 530–550 mμ and pH 4·25–5·00, with a solution containing $(0\cdot8–3\cdot2) \times 10^{-4}M$ reagent, 30% v/v ethanol and $(5–10) \times 10^{-4}M$ cetylpyridinium bromide, and for solutions containing $0\cdot1M$ pyridine, $2\cdot40 \times 10^{-4}M$ reagent and up to 19 ppm of uranium, for pH 4·55–4·95, measured against a reagent blank. The only effect of up to 30% v/v dimethylformamide is to change the slope of the 530 mμ calibration curve owing to the change in shape of the absorption spectrum. The own absorbance of the all reagent being in excess was always subtracted before plotting.

The molar absorptivity found from Lambert–Beer plots is $(1\cdot95–2\cdot02) \times 10^4$ at 530 mμ for solutions containing $0\cdot1M$ pyridine and excess of reagent. If dimethylformamide is used instead of ethanol the values are $1\cdot92 \times 10^4$ (540 mμ) and $1\cdot87 \times 10^4$ (530 mμ). The values agree in general with those from reagent concentration plots at pH 5·03 ($2\cdot03 \times 10^4$ at 530 mμ) or from the maximum absorbance of the pH plots for solutions with and without buffer, $(1\cdot96–2\cdot11) \times 10^4$ at pH 4·5–5·0. The sensitivity for $A = 0\cdot01$ is 0·116–0·126 μg/cm² at 530 mμ for solutions containing 30% ethanol and $0\cdot1M$ pyridine (pH 4·5–4·9).

Interferences

In solutions with $C_M = 2\cdot0 \times 10^{-5}M$ and $C_R = 2\cdot0 \times 10^{-4}M$, $0\cdot1M$ pyridinium nitrate buffer (pH 5·0) and $10^{-3}M$ cetylpyridinium bromide, it was found that $10^{-3}M$ sodium fluoride, $8 \times 10^{-3}M$ acetate, $3 \times 10^{-3}M$ carbonate and $1\cdot6 \times 10^{-2}M$ sulphosalicylic acid cause a deviation of −5% in the absorbance at 530 mμ, and that phosphate, citrate, oxalate, EDTA and CDTA interfere strongly.

Determination of uranium with TAMH

Similar considerations apply as in the case of the TAMR method, the differences being that λ_{max} is at 610–615 mμ, the reagent has negligible absorbance at 610 mμ up to pH 6, chelate hydrolysis shifts to lower pH values if the reagent concentration decreases, and absorbance is maximal at pH 5.25 if $C_R/C_M = 10$.

The molar absorptivity is $1\cdot45 \times 10^4$ at 610 mμ for unbuffered or pyridine buffered solutions with a large excess of reagent at pH 5·0. A slightly lower value, $1\cdot35 \times 10^4$ was found for nonbuffered solutions with $C_R = 2\cdot0 \times 10^{-4}M$ at pH 5·0, from the Lambert–Beer plot. The sensitivity is 0·18 μg/cm² for $A = 0\cdot01$ at 610 mμ and pH 5·0.

In solutions with $2\cdot0 \times 10^{-5}M$ uranium, $2\cdot0 \times 10^{-4}M$ reagent, $0\cdot1M$ pyridinium nitrate buffer (pH 5·0) and $10^{-3}M$ cetylpyridinium bromide, it was found that tartrate, citrate, oxalate, carbonate, EDTA, CDTA and phosphate interfere strongly, $2 \times 10^{-3}M$ sodium fluoride causes a deviation of −10%, and $3 \times 10^{-3}M$ acetate and $10^{-2}M$ sulphosalicylic acid cause a deviation of −5%.

A number of metal ions giving colour changes with TAMH and TAMR[21] cations interfere strongly, and previous separation of uranium is recommended if cations other than those of the alkali and alkaline earth metals are present. Beryllium and aluminium (up to amounts equivalent to 5 ppm of uranium) can be masked by $2 \times 10^{-3}M$ 5-sulphosalicylic acid.

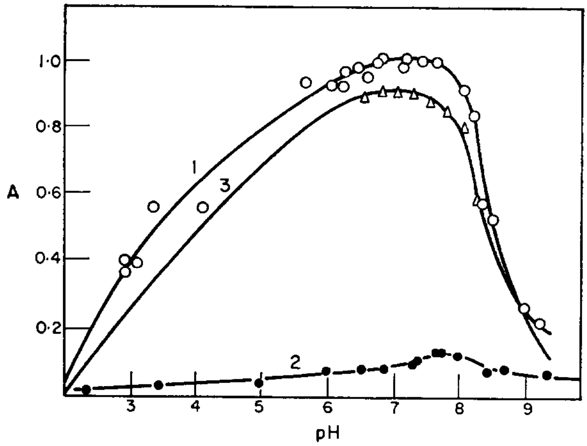

FIG. 9.—Plot of absorbance of extract *vs*. pH for the system UO$_2^{2+}$-TAMH in isobutyl methyl ketone.
$C_R = 4 \times 10^{-4}M$; $C_M = 2{\cdot}25 \times 10^{-5}M$; 0·1$M$ KNO$_3$; 0·05M tris buffer; 610 mμ.
1—$(A)_0 = f(\text{pH})_w$; *2*—reagent only; *3*—$\Delta(A)_0 = f(\text{pH})_w$.

Extraction of the TAMH chelate

The chelate and reagent are easily extracted into amyl alcohol or isobutyl methyl ketone, especially in the presence of potassium nitrate as salting-out agent, in a wide pH range up to pH 9. Chloroform is much less suitable, the chelate being partly collected at the interface.

The following procedure is recommended. To 10 ml of aqueous solution containing uranyl nitrate, potassium nitrate and 0·05M "tris" buffer, add at least an 18-fold excess of reagent ($C_R \sim 10^{-3}M$) and shake the mixture vigorously for 2–5 min with 10 ml of isobutyl methyl ketone. Separate the organic layer and centrifuge it for 2 min, and measure its absorbance at 610–640 mμ after 5 min.

The optimum pH is 6·5–7·5. The absorbance of the organic layer decreases rapidly at pH >7·6 owing to chelate hydrolysis, and is not reproducible over the pH interval 2·5–6 (Fig. 9). At pH ≤2 extraction is negligible. The chelate partly remains at the interface if the pH is <5.

"Tris" buffer, 0·05M, was suitable for adjusting the pH, large excesses of it having a negligible effect on the absorbance at pH ~7, for 15-fold excess of reagent. The minimum potassium nitrate concentration permissible is $2 \times 10^{-2}M$. Beer's law is obeyed for up to 5 ppm of uranium at 610–640 mμ, pH 7·05, $C_R = 4{\cdot}0 \times 10^{-4}M$, and 0·1$M$ potassium nitrate and 0·05M "tris" buffer in the aqueous phase. The reagent is also extracted into the organic layer and its absorbance must be corrected for by using a reagent blank as reference solution. Negative deviations from Beer's law were observed if the excess of reagent was lower than 18-fold. The molar absorptivity, $2{\cdot}09 \times 10^4$ at 610 mμ from the Lambert–Beer plot at pH 7·05 or $2{\cdot}08 \times 10^4$ at the same pH in the presence of 0·05M "tris", is larger than that for aqueous medium at pH 5·0. The sensitivity is 0·110 μg/cm^2 at 610 mμ for $A = 0{\cdot}01$.

Interferences

A number of common masking agents strongly interfere, when the optimum extraction conditions are used. A deviation of −5% is given at 610 mμ by $6 \times 10^{-3}M$

phosphate, $10^{-2}M$ acetate, $10^{-3}M$ oxalate, $1{\cdot}3 \times 10^{-3}M$ sulphosalicylate, $4 \times 10^{-3}M$ fluoride, $1{\cdot}6 \times 10^{-2}M$ CDTA or $8 \times 10^{-3}M$ tartrate. Citrate, EDTA and carbonate nterfere strongly at pH 7·0–7·2.

Composition of the extracted species

The plot of absorbance of the organic phase at 610 and 640 mμ *vs.* excess of reagent in the aqueous phase at pH 7·20 (0·2M sodium acetate), with or without the presence of 0·1M potassium nitrate, was interpreted according to Asmus's modified straight line method;[25] a 1:1 chelate appeared to be extracted under the given conditions. Acetate was added to prevent hydrolysis in solutions containing small excesses of reagent.

The number of solvent molecules attached to the metal chelate was determined by the same method for increasing concentrations of isobutyl methyl ketone, cyclohexane being used as diluent; only one molecule of isobutyl methyl ketone was found to be co-ordinated to the uranyl chelate.

The results showed that only the chelate $UO_2R{\cdot}NO_3{\cdot}$solvent was formed in the organic phase, but no evidence was found for the existence of a higher chelate even in the non-aqueous medium. Cyclohexane extracts the reagent but not the chelate. The reproducibility of absorbance readings for the organic layer decreases considerably for small concentrations of isobutyl methyl ketone in the organic layer. A 5-min extraction was found sufficient for equilibration at all concentrations of the active solvent. The organic layer becomes turbid if cyclohexane is added after the isobutyl methyl ketone, but not if it is added first.

Comparison to PAR and other TAR derivatives

Some data for the UO_2^{2+}-chelates with PAR and some TAR derivatives are collected in Table II.

TABLE II. —PAR AND SOME TAR DERIVATIVES AS REAGENTS FOR URANIUM(VI)

Reagent	λ max	$\varepsilon \, . \, 10^{-4}$	Sensitivity in μg/cm² for A = 0·01	pH
PAR	530	3·76	0·063	7–8*
TAR	530	3·18	0·072	7–8*
6-ethyl-TAR†	540	2·99	0·079	7–8*
6-methyl-TAR†	540	2·95	0·081	7–8*
6-propyl-TAR†	550	2·88	0·079	7–8*
TAMR‡	530	1·95	0·110	5·0§
TAMH‡	610	1·40	0·170	5·0§

* 0·2M tris/-hydroxymethyl/aminomethane buffer.
† 20% v/v dimethylformamide.
‡ 30% v/v ethanol.
§ 0·1M pyridinium nitrate buffer.

TAMR and TAMH do not reach the sensitivity of PAR and some *p*-dialkylamino derivatives of TAR[18,19,26] as reagents for Uranium(VI) but the TAMH —UO_2^{2+}-chelate has a suitable large colour contrast against the reagent blank.

Zusammenfassung—Die Komplexbildung von Uran(VI) mit 2-(2-Thiazolyl)-4-methoxyphenol (TAMH) und 2-(2-Thiazolylazo)-5-methoxyphenol (TAMR) wurde vergleichend untersucht. Die Komplexe sind weniger stabil und haben kleinere molare Extinktionskoeffizienten als die Komplexe mit PAR und TAR, sind aber für die Uranbestimmung trotzdem nützlich. Das Chelat mit TAMH kann in Isobutylmethylketon extrahiert werden. Beide Komplexe haben das Metall:Ligand-Verhältnis 1:1. Beim TAMH-Komplex ist $\log \beta_1 = 8{,}8$; $\varepsilon = 1{,}4 \times 10^4$ bei 610 nm; beim TAMR-Komplex $\log \beta_1 = 8{,}1$; $\varepsilon = 2{,}0 \times 10^4$ bei 530 nm.

Résumé—On a effectué une étude comparative de la complexation de l'uranium(VI) par le 2-(2-thiazolyl)4-méthoxyphénol (TAMH) et le 2-(3-thiazolylazo)5-méthoxyphénol (TAMR). Les complexes sont moins stables et ont des coefficients d'absorption moléculaire plus faibles que les complexes PAR et TAR mais ils sont encore utiles pour le dosage de l'uranium. On peut extraire le chélate TAMH en méthylisobutylcétone. Les deux complexes sont 1:1 métal:ligand. Pour le complexe TAMH, $\log \beta_1 = 8{,}8$; $\varepsilon = 1{,}4 \times 10^4$ à 610 mμ; pour le complexe TAMR $\log \beta_1 = 8{,}1$; $\varepsilon = 2{,}0 \times 10^4$ à 530 mμ.

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PHOTOMETRIC AND SPECTROCHEMICAL DETERMINATION OF GOLD IN IRON PYRITES, COPPER AND LEAD CONCENTRATES

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Summary—A photometric and a spectrochemical method have been developed for determining gold in iron pyrites, copper and lead concentrates. In both, the sample is dissolved and gold is extracted from 1*M* hydrochloric acid solution with a mixture of ethyl methyl ketone and chloroform (1:1). Gold was determined photometrically with *N,N'*-tetramethyl-*o*-tolidine. Conditions have been found for satisfactorily sensitive and reproducible spectral determination of gold. For this purpose the effect of various collectors and buffers on the evaporation curves of gold has been studied, as well as excitation conditions, form of the electrodes, optimum slit-width, and photographic variables. The sensitivity and precision of both methods have been evaluated.

CONSIDERABLE quantities of gold are obtained nowadays from iron pyrites, copper and lead concentrates. Their gold content varies from <1 to >10 g per ton. In rich concentrates gold is determined chiefly by the fire-assay method. In poorer ones (1–5 g/ton) this method has a number of drawbacks which lead to loss of time and materials and to doubtful results. On account of this, new methods were sought which would be simpler and give dependable results (see the review by F. E. Beamish[1]).

In the present work we offer two methods for the determination of gold in the raw materials mentioned, one photometric and the other spectrochemical. To achieve higher sensitivity and precision, an extractive concentration was used.

EXPERIMENTAL

Reagents

Standard solution of gold (100 μg/ml). Dissolve 0·0250 g of metallic gold in *aqua regia* and evaporate the solution on the water-bath to a dry residue. Dissolve the latter in 1*M* hydrochloric acid, transfer it into a 250-ml volumetric flask, and dilute to the mark with the same acid.

Tetrone. A 0·1% solution of *N,N'*-tetramethyl-*o*-tolidine in sulphuric acid (1 + 20).

Ethyl methyl ketone. Distil and use the 77–78·5° fraction.

Chloroform. Distil and use the 61–62·5° fraction.

Separation of gold by extraction

The gold-containing concentrates are conventionally dissolved in *aqua regia* and the solution obtained is alternately evaporated almost to dryness and reconstituted with hydrochloric acid, to give finally a solution of aurochloric acid.

Gold is mainly extracted with oxygen-containing agents such as diethyl ether, ethyl methyl ketone, ethyl acetate, acetylacetone, isobutyl methyl ketone, *etc.*[2-8] All these extract iron, arsenic, mercury, germanium, gallium, indium, thallium, molybdenum, *etc.* from hydrochloric acid.[10-14]

Amongst others, Jordanov and Havezov[15] have shown that the selectivity of separation can be increased by using a mixture of an extractive solvent and an "indifferent" diluent, the extraction being carried out at low acidity. By varying such solvent systems, we expected to find conditions under which gold could be extracted quantitatively while interfering elements would be extracted either not at all or to an insignificant degree.

We chose to investigate ethyl methyl ketone. It is cheap, easily obtainable, rather volatile, and in presence of "inert" solvents is practically insoluble in hydrochloric acid.

We studied the relationship between the distribution coefficient of gold and the acidity. Both phases had a volume of 10 ml and were mutually saturated for each of the chosen acidities. We found that the distribution equilibrium for gold in the two phases is established in 2 min.

Experiments showed that from a practical stand-point, it is easiest to work with a medium of 1*M* hydrochloric acid; the distribution coefficient is high enough to allow the quantitative transfer of gold to the organic phase in a single extraction and the separation of the two phases is very fast.

Mixtures of ethyl methyl ketone with chloroform or carbon tetrachloride were studied as extractants. The best mixture was ethyl methyl ketone and chloroform, 1:1, which extracts gold quantitatively in a double extraction, but not the main components, iron, copper and lead.

Photometric determination of gold

The concentrates are dissolved, and the gold is extracted and determined photometrically with tetrone.[16]

Weigh 0·5–2·0 g of copper, lead or pyrites concentrate in a porcelain crucible and heat in an electric furnace at 700° for 40 min to remove flotation reagents and oxidize the sulphide. Cool the sample, add 10–15 ml of freshly prepared *aqua regia*, let stand for 1–2 hr and then heat on a sand-bath to complete the decomposition. Evaporate almost to dryness and add 5 ml of concentrated hydrochloric acid, and repeat (the first time on the sand-bath, and the second on the water-bath). Dissolve the dry residue in 30 ml of 1*M* hydrochloric acid, transfer the solution into a 50 or 100-ml volumetric flask, and dilute to the mark with the same acid. Silicic acid falls to the bottom of the flask. From the clear solution, transfer 10 or 20 ml with a pipette into a separating funnel, and extract twice with 10-ml portions of a mixture of ethyl methyl ketone and chloroform (1:1). Wash the combined extracts in another separating funnel with 10 ml of 1*M* hydrochloric acid. Transfer the washed extract into a porcelain crucible, evaporate it to a dry residue under an infrared lamp and heat it in an electric furnace at 700° to decompose the organic matter completely. Wet the dry residue with 10–15 drops of *aqua regia* (cover with a clock glass) and heat for 15 min, then evaporate almost to dryness. Add 4–5 drops of hydrochloric acid and again evaporate almost to dryness. Add 1 ml of 0·1% tetrone solution, leave for 10 min to develop the colour, dilute to 10 ml, and measure photometrically at 480 mμ. Prepare a calibration curve for the range 2–10 mg of gold.

Spectrochemical determination of gold

Various methods are known for the spectrochemical determination of gold in rocks, ores, and ore concentrates.[17–20] According to most of these, gold must previously be separated from the other elements present, by use of collectors of various kinds, ion-exchange methods, *etc.* For us the problem consisted of finding a convenient way of quantitatively transferring the gold from the organic extract to the carbon electrode. To this end several substances were tested, which had to be good collectors and at the same time allow the most sensitive possible determination of gold.

The substances tried were silicon dioxide, lead oxide, magnesium oxide, strontium sulphate, aluminium powder, and inactive and activated carbon. Various forms of electrodes were used: hollow electrodes with craters of various depths and diameter, as well as cup-shaped ones with a cup of various dimensions. The second electrode ended in a hemisphere. The electrode holders were water-cooled. The most appropriate slitwidth was found by measuring the diffusion halation in the photoplate.[21,22] For all collectors, the evaporation curves of gold (with varying weight of the sample) were measured at a current strength of 10, 12, 14, 16 and 18 A. Experiments showed that with all collectors the best results are obtained at a current strength of 16 A, a slit of 16 μ, width of the intermediate diaphragm 3·2 mm, sample weight 10 mg, and an electrode crater 4 mm in diameter and 3 mm deep. Figures 1 and 2 show the evaporation curves. The spectra were photographed on Blau Hart plates, and the Au I line at 2675·95 Å was measured photometrically.

The most suitable base proved to be carbon powder. Whether it was activated or not, the evaporation curves were the same (Fig. 2); full evaporation takes place within 40–50 sec. Activated carbon, however, has the advantage of being a better collector.

Figure 3 shows the calibration curves with bases of activated carbon powder and lead sulphate. The reproducibility with these two bases, expressed by the standard deviation *S* and the coefficient of variation *V* at the 95% confidence level (20 determinations) is: $PbSO_4$, *S* 6·3, *V* 16%; carbon, *S* 2·6, *V* 4%.

The reproducibility when powdered carbon is used fully answers the practical requirements.

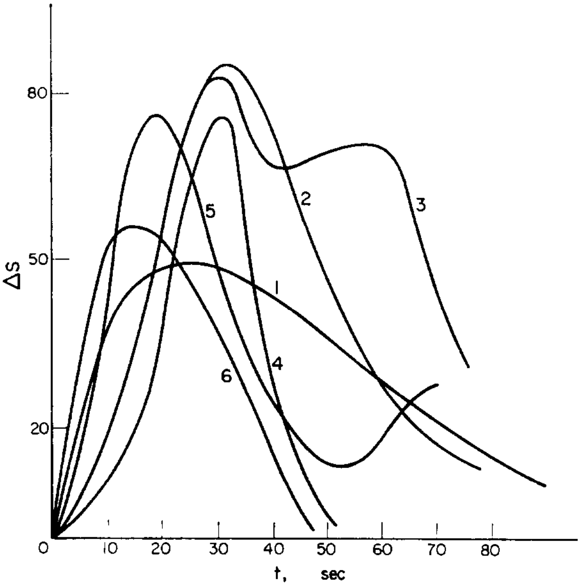

FIG. 1.—Evaporation curves for gold; the collectors are 1—SiO_2, 2—$SrSO_4$, 3—PbO, 4—$PbSO_4$, 5—Al, 6—MgO. ΔS is the intensity of the measured line relative to background intensity.

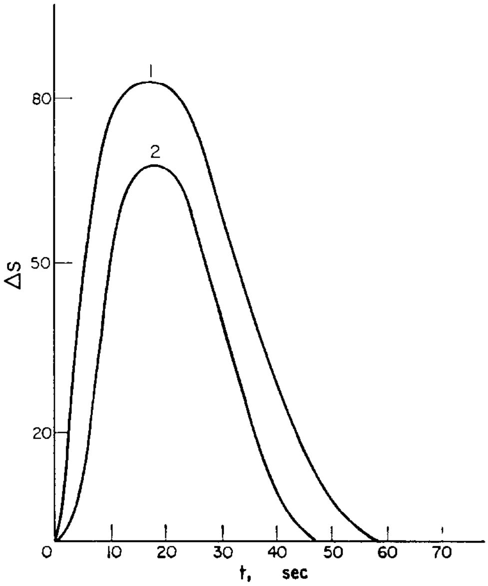

FIG. 2.—Evaporation curves for gold; the collectors are 1—activated carbon, 2—inactive carbon.

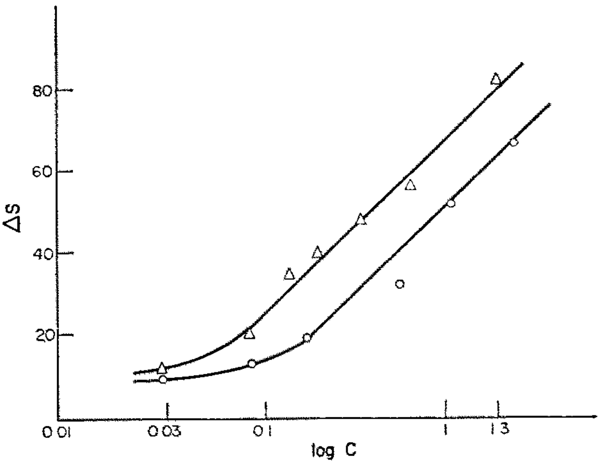

Fig. 3.—Calibration curves for gold; the collectors are Δ—activated carbon, ○ lead sulphate. Blauhart plates.

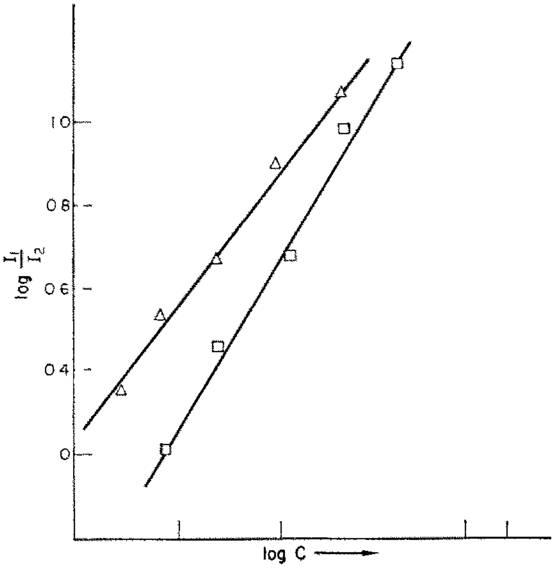

Fig. 4.—Calibration curves for gold; the collectors are □—activated carbon, Δ—activated carbon containing 10% NaCl. 3C plates.

Attempts to increase the sensitivity

Further studies were aimed at increasing the sensitivity of the determination. This could represent one more variation of the method, to be used when necessary. The possibilities were to use photoplates with higher sensitivity, and to add buffering substances to the collector to stabilize the temperature of the plasma.

The plates tested were Russian (type 3C; $\gamma = 1{\cdot}50$–$1{\cdot}70$) and Blau Hart (ORWO, German Democratic Republic; $\gamma = 1{\cdot}15$–$1{\cdot}18$). They have the same sensitivity in the 2600–3100 Å region.

The excitation potential of the Au I line at 2675·95 Å is 4·6 eV, and that of the Au I line at 2427·95 Å is 5·1 eV. Taking these data into account, we chose sodium chloride as an appropriate buffer; the ionization energy of sodium is 5·13 eV. In presence of sodium chloride, the maintained temperature of the plasma will be very close to the optimum temperature of excitation for these gold lines. The experimental results, shown in Fig. 4, confirmed our suppositions.

The determination limits under the optimum working conditions, for the Au I line at 2675·95 Å are 0·003 μg for 3C plates and 0·02 μg for Blau Hart plates.

Method of analysis. Dissolve the sample and extract the gold as in the photometric method. Transfer the extract to a porcelain dish, add 40 mg of activated carbon powder containing 10% of sodium chloride and evaporate the mixture to dryness. Homogenize the residue and place 10-mg samples in three graphite electrodes with craters 4 mm in diameter and 3 mm deep. Excite the spectra in an electric arc at a current of 16 A, and photograph with 60 sec exposure, intermediate diaphragm 3·2 mm, and slit 16 μ. Prepare a standard curve, each point being the average of three determinations.

RESULTS

Both methods were tested by determination of the gold content of a copper concentrate. The results obtained are shown in Table I.

TABLE I

Method	No. of determinations	Mean Au content, *g/ton*	Std. devn. *g/ton*
Photometric	12	2·83	0·18
Spectrochemical	13	2·72	0·13

The average result from a determination of gold in the same concentrate by the fire-assay method was 2·8 g/ton

The methods are intended for use with the types of sample specified, or other gold-bearing materials from which the gold is completely extractable with *aqua regia*, and are not applicable to other types of material.

Zusammenfassung—Eine photometrische und eine spektrochemische Methode zur Bestimmung von Gold in Eisenpyriten sowie Kupfer- und Bleikonzentraten wurden entwickelt. Bei beiden wird die Probe gelost und Gold aus 1*M* salzsaurer Lösung mit einer 1:1-Mischung aus Äthylmethylketon und Chloroform extrahiert. Gold wurde photometrisch mit N,N′-Tetramethyl-*o*-toluidin bestimmt. Bedingungen für eine befriedigend empfindliche und reproduzierbare spektrale Bestimmung von Gold wurden ebenfalls gefunden. Zu diesem Zweck wurde der Einfluß verschiedener Sammler und Puffer auf die Verdampfungskurven von Gold untersucht sowie die Anregungsbedingungen, Elektrodenform, optimale Spaltbreite und photographische Variable. Empfindlichkeit und Genauigkeit der Methoden wurden bestimmt.

Résumé—On a élaboré une méthode photométrique et une méthode spectrochimique pour doser l'or dans les pyrites de fer, le cuivre et les concentrats de plomb. Dans les deux cas, on dissout l'échantillon et extrait l'or à partir d'une solution 1*M* en acide chlorhydrique par un mélange de méthyl-éthylcétone et de chloroforme (1:1). On a dosé l'or photométriquement par la N,N′-tétraméthyl-*o*-tolidine. On a trouvé des conditions de détermination spectrale de l'or de sensibilité et reproductibilité satisfaisantes. Dans ce but, on a étudié l'influence de divers collecteurs et tampons sur les courbes d'évaporation de l'or, ainsi que les conditions d'excitation, la forme des électrodes, la largeur de fente optimale et les variables photographiques. On a évalué la sensibilité et la précision des deux méthodes.

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SEPARATION OF FLUORIDE BY RAPID DIFFUSION USING HEXAMETHYLDISILOXANE*

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Summary—The presence of hexamethyldisiloxane greatly accelerates the diffusion separation of fluoride, making it possible to recover >97% of radioactive fluoride in one hour at room temperature. Agitation, and concentration of the acid and alkaline solutions, affect the rate of diffusion. The presence of biological material has little effect on the rate of diffusion. Sulphate and phosphate do not diffuse under these conditions.

SEPARATION is a necessary first step in the determination of fluoride in most types of samples. However, the available techniques are either tedious or time-consuming, and for some materials, unreliable.

Steam-distillation of hydrogen fluoride or hydrogen hexafluorosilicate from acid solutions has been the method of choice for many years, but it suffers from the tendency of the distillates to be contaminated with phosphoric or sulphuric acid [1,2] and from the loss of hydrogen fluoride by reaction with the glass vessels.[3] Avoidance of phosphoric or sulphuric acid in the distillate is crucial because the available reagents generally react with sulphate and phosphate.[1] Control of these contaminants depends in part on very close temperature regulation, which is difficult. The distillation procedure in any case is not adaptable to determination of large numbers of samples on a routine basis.

Diffusion procedures have become widely used because many more samples can be dealt with at one time and high temperatures are not required. Temperatures of 60° eliminate contamination by phosphoric or sulphuric acid and make possible the use of plastic dishes, avoiding any reaction between hydrogen fluoride and glass. However, there is evidence that diffusion at this temperature may not be satisfactory for serum analysis,[4] and in any case requires at least 12 hr to reach completion.[5]

The recent discovery that diffusion of fluoride is greatly accelerated by the presence of silicone grease used as a sealant of the microdiffusion dishes[6] has led to the development of a new procedure for the rapid diffusion of fluoride at room temperature, using hexamethyldisiloxane (HMDS), the simplest silicone, $[(CH_3)_3Si]_2O$.

EXPERIMENTAL

Apparatus

Non-wettable diffusion dishes obtained direct from Falcon Plastics, 5500 West 83rd Street, Los Angeles, California 90045 were used for 1–2 ml samples. The generally available Falcon microdiffusion dishes have wettable surfaces which give high blank values with the Morin–thorium reagent[7] and may allow premature mixing of solutions placed in the outer compartment.

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Polystyrene Petri dishes (Falcon Plastics) were used for 10-ml samples. The trapping solution was put in pH-meter sample cup covers (p 207·0005, Mallinckrodt Chemical Works) which were placed in slightly larger cups, obtained by breaking out the centre compartment of the disposable Falcon dishes, and floated on the acidified sample (Fig. 1).

A "Gyrotory Shaker", New Brunswick Scientific Company, Box 606, New Brunswick, New Jersey, was used to give 80 cpm rotary motion with ½-in. throw.

A well-type sodium iodide crystal counter was used for counting the $^{18}F^-$ and a liquid scintillation counter was used for the ^{14}C, $^{32}PO_4^{3-}$ and $^{35}SO_4^{2-}$.

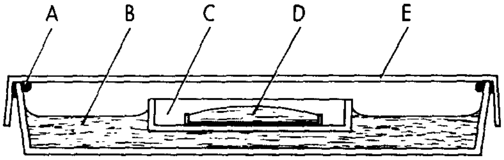

FIG. 1—Diffusion apparatus.
A—Vaseline seal; B—acidified sample; C—plastic cup; D—trapping solution; E—lid

Materials

Radioactive fluoride, $^{18}F^-$, carrier-free, was obtained from Western New York Nuclear Research Center, Power Drive, Buffalo, New York. The only gamma-emitting contaminant detected[8] was $^{82}Br^-$. The error due to $^{82}Br^-$ contamination was checked by counting duplicate samples after 24 and 48 hr and comparing the observed changes with those expected from pure $^{18}F^-$, which has a half-life of 109·5 min.[9] The error at 24 hr was 0·2%. The longest elapsed time in the following experiments was 25 hr. The amount of $^{19}F^-$ added with the $^{18}F^-$, as estimated by the method described in a companion article,[7] was less than 1 nmole.

Uniformly labelled carbon-14 hexamethyldisiloxane (HM*DS), activity 1 mC/g, was obtained from Dow-Corning, Midland, Michigan. Counting of ^{14}C, $^{32}PO_4^{3-}$ and $^{35}SO_4^{2-}$ was done in a liquid scintillation counter with Bray's solution.[10] The standards were prepared so that they contained the same solution components as the counted samples, to avoid systematic quenching errors.

The HMDS (Dow Corning 200 Fluid, 0·65 centistokes, Dow Corning, Midland, Michigan) was introduced as its saturated solution in 6*M* hydrochloric acid, stored with excess of HMDS in a separatory-funnel.

Lead-free 70% perchloric acid (11·4 *M*) was obtained from the Frederick G. Smith Co., Columbus, Ohio.

Procedure

The trapping solution and acidified sample are placed in the centre and outer compartments respectively. The lids are sealed with petroleum jelly (Vaseline). Because of the volatility of HMDS all samples are brought to this stage before proceeding.

The silicone solution, 0·5 ml of HMDS-saturated 6*M* hydrochloric acid is introduced into the outer compartment through a 1-mm hole in the lid and the hole is quickly covered with Vaseline. Unless otherwise stated, all samples were agitated by rotary motion. The trapping solution was transferred by means of a plastic pipette to a plastic test-tube for counting. Serum supernatant was prepared by centrifuging serum with an equal volume of 6·8*M* perchloric acid to precipitate the proteins.

The recovery of $^{18}F^-$ was determined by comparison with radioactive standards. The samples and standards were counted within a half-hour of each other to minimize the amount of correction needed for radioactive decay.

RESULTS

Tables I, II and III show the effect of variables such as the trapping agent, rotary motion and the amount of acid on the rate of $^{18}F^-$ diffusion. In order to detect differences in behaviour, a 10-min ± 15-sec diffusion time was used so that the process would not be completed.

Table I shows that sodium hydroxide is more effective as a trapping solution than is sodium carbonate. However, even the sodium carbonate which had picked up

TABLE I—EFFECT OF TRAPPING SOLUTION ON RECOVERY OF $^{18}F^{-}$*

Trapping solution	No. of samples	Recovery, %
3 ml 0·1*M* NaOH	6	91–95
3 ml 0·1*N* Na_2Co_3	6	68–81
3 ml 0·1*N* Na_2Co_3, pH 9·8	5	77–79
3 ml 0·1*N* Na_2Co_3, pH 10·8	5	85–89
3 ml 0·03*N* Na_2Co_3	4	75–76
1 ml 0·1*N* Na_2Co_3 + 0·5 ml C_2H_5OH	4	82–85

* The outer compartment contained 3 ml of 3·4*M* $HClO_4$, 15 nmole of NaF labelled with $^{18}F^{-}$, and 0·5 ml of silicone-saturated 6*M* HCl. Diffusion for 10 min.

TABLE II—EFFECT OF HMDS AND AGITATION ON RECOVERY OF $^{18}F^{-}$*

Agitation time, *min*	Sample solution	No. of samples	Recovery, %
10	non-siliconed HCl added	4	0·4–0·5
0	silicone-saturated HCl separate from sample	3	33–34
0·25	silicone-saturated HCl	5	55–63
10	silicone-saturated HCl agitated with sample for full time	4	81–84

* The outer compartment also contained 3 ml of 3·4*M* $HClO_4$ and 15 nmole of NaF labelled with $^{18}F^{-}$. The trapping solution was 1 ml of 0·1*N* Na_2CO_3 in 20% ethanol. Diffusion for 10 min.

TABLE III—EFFECT OF AMOUNT OF ACID AND SAMPLE ON RECOVERY OF $^{18}F^{-}$*

Sample solution	No. of samples	Recovery, %
1 ml H_2O	5	67–69
1 ml H_2O + 1 ml 6·8*M* $HClO_4$	5	79–82
1 ml H_2O + 2 ml 6·8*M* $HClO_4$	4	80–85
1 ml urine + 1 ml 6·8*M* $HClO_4$	3	76–81
3 ml serum supernatant	3	68–72

* The outer compartment also contained 0·5 ml of silicone-saturated 6*M* HCl. The trapping solution was 1 ml of 0·1*N* Na_2CO_3 in 20% ethanol. Diffusion for 10 min.

enough carbon dioxide from the air for its pH to be reduced to 9·8 was efficient enough to recover over 75% of the fluoride in 10 min. Sodium carbonate was used in subsequent experiments because exposure to carbon dioxide is not critical, as it is with sodium hydroxide (which also causes instability of the fluorescence of the Morin-thorium reagent[7]).

Table II shows the effect of HMDS on the rate of diffusion. Without the HMDS there is practically no diffusion of fluoride. When the HMDS-saturated hydrochloric acid is present but not in contact with the sample one-third of the fluoride diffuses to the trapping solution in 10 min, owing to the volatilization of the HMDS, illustrating the necessity of introducing the HMDS into the system through a small hole in the already sealed lid. Mixing the solutions increases the rate of diffusion appreciably and continuous rotary motion results in over 80% recovery in only 10 min.

Table III shows that the addition of perchloric acid to the sample increases the rate of diffusion in spite of the fact that the volume of the solution from which the fluoride is being diffused is larger. Urine has little or no effect on the rate of diffusion. Serum supernatant appears to reduce it slightly.

Table IV shows that about 98% of added radioactive fluoride can be recovered from bone, urine or serum supernatant in 1–6 hr. The time required depends on whether alcohol is used to spread the trapping solution and rotary agitation is used, and on the sample size.

TABLE IV—COMPLETENESS OF $^{18}F^-$ RECOVERY

Trapping solution*	Motion	Time, hr	Sample†	No. of samples	Recovery, %
Ethanol	Rotary	1	1 ml urine + 1 ml 6·8M $HClO_4$	5	99·3 ± 1·2‡
Ethanol	Rotary	1	10 mg bone¶ + 2 ml 3·4M $HClO_4$	5	98·5 ± 1·1
Ethanol	Rotary	1	10 mg bone¶ + 2 ml 3·4M $HClO_4$	5	97·9 ± 2·6
Ethanol	Rotary	1	3 ml serum supernatant	5	100·5 ± 1·1
Water	Rotary	1	4 ml serum supernatant	5	98·0 ± 1·0
Water	Rotary	2	4 ml serum supernatant	5	98·4 ± 1·8
Water	Static	2	4 ml serum supernatant	5	97·2 ± 2·9
Water	Static	3	4 ml serum supernatant	5	99·4 ± 1·1
Water	Rotary	2	20 ml serum supernatant	5	94·8 ± 0·5
Water	Rotary	6	20 ml serum supernatant	5	98·1 ± 0·5

* 1 ml 0·1N Na_2CO_3 in either 20% ethanol or in water.

† The outer compartment also contained 0·5 ml of silicone-saturated 6M HCl.

¶ Stable fluoride analysis by Taves's method[7] and by method of Singer and Armstrong (*Anal. Biochem.*, 1965, **10**, 495) showed 70 nmole of F in the first sample and 4500 nmole in the second.

‡ Relative standard deviation.

Most lots of hydrocholoric acid are contaminated with appreciable amounts of fluoride so it was of interest to determine whether the trimethylfluorosilane formed by the addition of HMDS might not be extracted into the excess of HMDS on top of the acid in the storage funnel. This was done by measuring the $^{18}F^-$ distribution after shaking HMDS with 6M hydrochloric acid containing $^{18}F^-$. It was found that only 0·04% was left in 50 ml of acid after two extractions with 10 ml of HMDS. The distribution ratio was greater than 100:1.

Carbon-14 labelled HMDS (HM*DS) was used to determine the distribution of HMDS in the diffusion process and in subsequent steps for the analysis of stable fluoride. The concentration of HM*DS in the saturated 6M hydrochloric acid, as measured by its radioactivity, was 0·0016M. To determine how much of the HMDS transfers to the trapping solution, 0·5 ml of the HM*DS solution (800 nmole) was placed in the outer chamber of a diffusion dish with 4 ml of 3·4M perchloric acid. In 30 min, 110 and 120 nmole (duplicate experiments) were recovered in the trapping solution (0·1N sodium carbonate in 20% v/v alcohol). Replacing the trapping solution and diffusing for another 30 min resulted in the recovery of 62 and 68 nmole of HM*DS. The trapping solution, when titrated with hydrochloric acid, as necessary for analysis of stable fluoride, showed no loss of HM*DS. However, when the trapping solution (not titrated) was evaporated, 99% was lost from each of 4 samples.

The possibility that phosphate or sulphate diffuses with the HMDS to contaminate the trapping solution was tested by using 2 ml of 0·002M phosphate containing 1×10^7 cpm $^{32}PO_4^{3-}$ and 2 ml of 0·01M sulphate with 9×10^7 cpm $^{35}SO_4^{2-}$ as the samples (5 sets of each). After 2 hr in the usual procedure for diffusion not more than a millionth of the phosphate or sulphate had diffused. The background was 63 cpm and the samples 63 ± 4 and 70 ± 6 cpm respectively (standard errors shown).

DISCUSSION

The use of HMDS makes it possible to separate fluoride from samples by diffusion at room temperature in 1 hr, less than a tenth of the time taken by any previous diffusion method.

HMDS is presumed to accelerate the diffusion of fluoride by the formation of trimethylfluorosilane (TMFS):[11]

$$HF + (CH_3)_3SiOSi(CH_3)_3 \rightarrow (CH_3)_3SiF + (CH_3)_3\,SiOH \qquad (1)$$

$$HF + (CH_3)_3SiOH \rightarrow (CH_3)_3SiF + H_2O \qquad (2)$$

In the absence of a silicone the hydrogen fluoride will react with itself and with water to form higher molecular weight complexes, which explains why the constant boiling temperature[12] of hydrofluoric acid is 112° whereas hydrogen fluoride boils at $-80°$. On the other hand, the TMFS (b.p. 16·4°)[13] would be expected to be hydrophobic and retain its volatility, thus providing a means for fluoride to escape from an acid solution. The release of fluoride when the TMFS comes in contact with the alkaline trapping solution is expected from reversal of reaction 2 by hydrolysis, assisted by condensation of silanol to form the parent HMDS:

$$2(CH_3)_3SiOH \rightarrow [(CH_3)_3Si]_2O + H_2O. \qquad (3)$$

To the extent that the reformed HMDS or possibly the silanol returns to the acid solution and enters the cycle again, the whole process becomes catalytic. Evidence that this occurs is shown in Table IV; 800 nmole of HMDS resulted in diffusion of 4500 nmole of fluoride from bone in 1 hr.

The suggested hydrolysis and condensation mechanism may explain the greater over-all diffusion rates when a stronger alkali is used. However, there may also be a direct substitution reaction of OH^- for F^- on the trimethylsilyl group. The increased rate of diffusion with the addition of acid is probably due to the resultant decrease in the activity of the water which in turn decreases the reaction of hydrogen fluoride with water and makes hydrogen fluoride more available for the reaction with HMDS. The fact that agitation increases the speed of the process suggests that the rate of diffusion in solution becomes a limiting factor as a result of the marked increase in the rate of escape of fluoride from the surface.

Most previous methods have unwittingly employed silicone-aided diffusion of fluoride by using silicone grease to seal the diffusion dishes. A previous study has indicated that the silicone grease supplies a volatile component, possibly HMDS, since the grease could be placed some distance away from the acid and still produce its effect.[6] However, since higher temperatures and longer times were needed it was apparently not supplied in great enough quantities for maximum effectiveness. Under conditions where diffusion is limited by the supply of volatile silicone, factors such as acid strength and agitation would appear to be unimportant, thus explaining why Wharton[5] saw little or no effect from these factors.

Diffusion at room temperature, rather than at 55–60°, is an advantage because it decreases the likelihood than other volatile components will contaminate the trapping solution. The possibility that sulphate and phosphate might be diffusing with HMDS in the same manner as fluoride was ruled out by the experiments with $^{32}PO_4^{3-}$ and $^{35}SO_4^{2-}$.

A question not settled here is whether the silicone present after titration of the trapping solution will adversely affect the reagents used for the measurement of fluoride. (This is not a problem with the Morin-thorium reagent.[7]) The silicone can be removed by evaporating the trapping agent, but this is not ideal since it takes at least an hour and exposes the samples to possible contamination from the air. Extraction of $^{18}F^-$ from hydrochloric acid into a layer of HMDS indicates that TMFS is soluble in organic solvents, as would be expected. This finding might prove useful in collecting fluoride from some types of large samples for analysis. The increased ability to diffuse fluoride makes it possible to use larger samples of serum (10 ml) than have been previously reported. This is important because it allows sufficient concentration of fluoride from serum for results to be checked by more than one method.

Acknowledgement—I wish to thank Mrs Barbara Huggins for her technical assistance.

Zusammenfassung—Die Gegenwart von Hexamethyldisiloxan beschleunigt die Diffusionsabtrennung von Fluorid beträchtlich und ermöglicht die Wiedergewinnung von über 97% radioaktivem Fluor in einer Stunde bei Raumtemperatur. Die Diffusionsgeschwindigkeit wird durch Rühren sowie die Konzentration der sauren und alkalischen Lösungen beeinflußt. Die Anwesenheit von biologischem Material hat auf die Diffusionsgeschwindigkeit nur geringen Einfluß. Sulfat und Phosphat diffundieren unter diesen Bedingungen nicht.

Résumé—La présence d'hexaméthyldisiloxane accélère fortement la séparation par diffusion du fluorure, rendant possible la récupération de plus de 97% de fluorure radioactif en une heure à température ordinaire. L'agitation et la concentration des solutions acides et alcalines influent sur la vitesse de diffusion. La présence de matière biologique a peu d'effet sur la vitesse de diffusion. Le sulfate et le phosphate ne diffusent pas dans ces conditions.

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SHORT COMMUNICATIONS

Activation analysis for selenium and tellurium trace impurities in gallium, arsenic and gallium arsenide

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THE reported methods and data[1–5] for the radiochemical separation of selenium and tellurium show that for the activation analysis of selenium either the 120-day ^{75}Se or the 17·5-sec ^{77m}Se activity can be used, and for tellurium the 25-min ^{131}Te, 74-min ^{129}Te, 9·3-hr ^{127}Te or the 104-day ^{123m}Te activities. ^{75}Se and ^{77m}Se have a large cross-section for neutron capture and an energy spectrum very suitable for measurement. The measurement can be disturbed by the secondary reactions

$$^{75}\text{As}(\text{n}, \gamma)^{76}\text{As} \xrightarrow[26\cdot5\ \text{hr}]{\beta^-} {}^{76}\text{Se}(\text{n}, \gamma)^{77m}\text{Se}$$

$$^{75}\text{As}(\text{n}, 2\text{n})^{74}\text{As} \xrightarrow[18\ \text{day}]{\beta^-} {}^{74}\text{Se}(\text{n}, \gamma)^{75}\text{Se}$$

Evaluation[6–8] of the secondary reaction yield shows that under the experimental conditions used the secondary selenium yield can be ignored down to concentrations of 10^{-8} g of selenium per g of arsenic.

EXPERIMENTAL

Reagents

Solvent and carrier solution: 150 ml of 65% nitric acid, 150 g of tartaric acid, 10 mg of selenium and 10 mg of tellurium, diluted with distilled water to 1000 ml.

Reducing solution: 1% hydrazine sulphate in water.

Buffer: 50 g of tartaric acid, 10 g of EDTA and 10 g of potassium dihydrogen phosphate diluted with distilled water to 1000 ml.

Dithizone solution: 0·002*M* in carbon tetrachloride purified by extraction with ammonium hydroxide.

Diethylammonium-*N*,*N*-diethyldithiocarbamate solution: 0·04% in carbon tetrachloride.

Irradiation

In the core of the VVRS reactor, with a thermal neutron flux of about $1\cdot5 \times 10^{13}$ n.cm^{-2}.sec^{-1}. For chemical separation, 0·5-g samples in quartz ampoules were irradiated for 48 hr. For non-destructive analysis, 0·5-g samples in quartz ampoules were irradiated for 116 hr, or, in the fast procedure, 0·2-g samples in polyamide holders were irradiated for 20 sec.

Destructive method

The activated samples and standards were dissolved by slow warming in 10 ml of the solvent and carrier solution, and cooled. Then 2 ml of reducing solution were added and the mixture put in the extractor (Fig. 1) containing 10 ml of dithizone solution. After mixing for 2 min, the organic phase was collected and the extraction repeated with 10 ml of dithizone solution. The organic phases, containing both the selenium and tellurium activities, were combined and removed from the hot-chamber for further separation. After evaporation of the solvent, the chelate complexes were destroyed by the addition of a few drops of sulphuric–perchloric acid mixture. To the clear solution 15 ml of buffer solution were added and the pH was adjusted to 8·5 with 2*M* potassium hydroxide. Tellurium was then extracted by shaking for 2 min each time with two 10-ml portions of diethylammonium-*N*,*N*-diethyldithiocarbamate solution. The selenium remains in the aqueous phase. The standards were treated throughout in the same way. The tellurium activity was measured at lower concentrations by liquid GM-counter, at higher concentrations by gamma-spectrometer. The selenium activity was measured by gamma-spectrometer.

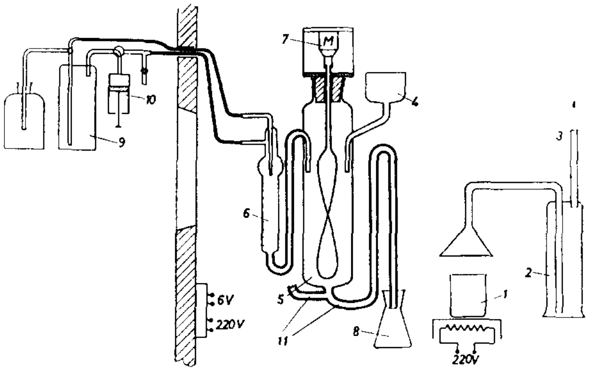

FIG. 1.—Extraction assembly.
1—Dissolving; *2*—active vapour absorber; *3*—evaporating; *4*—inlet for active sample; *5*—extractor; *6*—solvent feeder; *7*—stirring motor; *8*,*9*—solvent containers; *10*—hand-controlled piston; *11*—gooseneck capillaries.

Non-destructive analysis

After short irradiation by means of the pneumatic facility[9] and 40–45 sec cooling, the ^{77m}Se activity of the sample was measured by taking the gamma-spectrum repeatedly in the range from 0 to 300 keV. The 120-day ^{75}Se activity was measured after cooling for 2–3 months. The gamma-spectra were taken in the range from 0 to 700 keV and were evaluated by Covell's method.[10]

The non-destructive method was found to be inadequate for the determination of tellurium, since in the measured gamma-spectrum, even after long cooling, only the 159-keV energy peak of ^{123m}Te could be identified, with poor sensitivity.

RESULTS

The degree of extraction was determined for both impurities by varying the stirring times and dithizone concentrations. The metal complex formation rate is markedly dependent on the hydrogen ion concentration in the aqueous phase. In dilute acidic solutions the rate of equilibration was found to be slow and proportional to the dithizone concentration, in agreement with previous observations.[11] With optimum mixing time, *i.e.*, 2–3 min, and dithizone in excess of the minimum 50-fold molar ratio needed (relative to inactive carrier), selenium and tellurium are extracted almost quantitatively. Possible co-extraction of Ag, Hg, Pd and Cu,[12] though not observed in the test samples, is not expected to interfere with the selenium determination if the gamma-spectra are

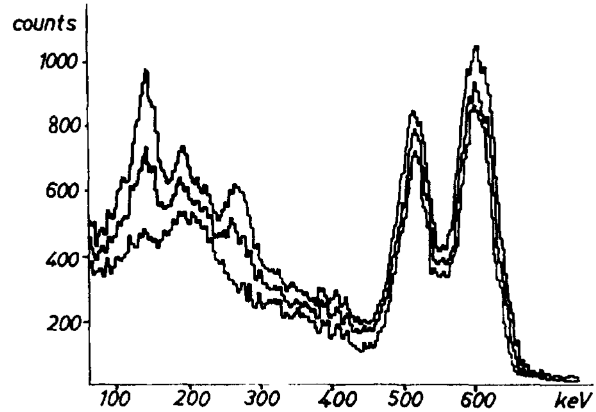

FIG. 2.—Gamma-spectra of 0·7-g As sample containing: *1*—7 × 10^{-8} g of Se; *2*—3 × 10^{-8} g of Se; *3*—no Se.
Irradiation time 116 hr, cooling time 108 days, measuring time 2000 sec.

taken at different times. In a double extraction 91 ± 3% of the tellurium and selenium passes into the organic phase. No activity loss due to dissolution or complex destruction was observed. In the separation of tellurium from selenium, 4–5% of the tellurium activity is lost. Thus, about 90% of the selenium and 85% of the tellurium can be isolated.

The sensitivity by the destructive method was found to be 10^{-8} g, with ±20% error, for both impurities. The sensitivity of the non-destructive method utilizing the 160-keV ^{77m}Se activity is 10^{-6} g (±30% error) as compared with 5×10^{-8} g (±30%) obtainable from ^{75}Se. The latter procedure, however, requires cooling times from 2 to 3 months to eliminate the interference from ^{74}As (Fig. 2). Tellurium can be determined under the same conditions down to 10^{-6} g (±30%) from the 159 keV ^{123m}Te activity if the selenium contamination of the sample is less than 5×10^{-8} g.

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Summary—Destructive and non-destructive activation analysis for selenium and tellurium has been studied. In destructive analysis the selenium and tellurium activities are co-extracted from the irradiated and dissolved matrix elements with dithizone/CCl_4 reagent in a hot-chamber by remote manipulation, then separated from each other by diethylammonium-*N*,*N*-diethyldithiocarbamate/CCl_4 extraction, tellurium going into the organic phase and selenium being retained by the aqueous phase. The sensitivity of the method is 10^{-8} g for both elements. By non-destructive methods, selenium can be determined down to 10^{-6} g on short irradiation, and down to 3×10^{-8} g on long irradiation and cooling, and tellurium down to 10^{-6} g with long irradiation and cooling.

Zusammenfassung—Die aktivierungsanalytische Bestimmung von Selen und Tellur mit und ohne Zerstörung wurde untersucht. Bei der zerstörenden Analyse werden die Selen- und Tellur-Aktivitäten gemeinsam aus den bestrahlten und gelösten Begleitelementen mit Dithizon/CCl_4 in einer "heißen Kammer" mit Fernbedienung extrahiert; dann werden sie durch Extraktion mit Diäthylammonium-*N*,*N*-diäthyldithiocarbamat/CCl_4 voneinander getrennt, wobei Tellur in die organische Phase geht und Selen in der wäßrigen Phase bleibt. Für beide Elemente beträgt die Empfindlichkeit der Methode 10^{-8} g. Mit zerstörungsfreien Methoden läßt sich Selen bei kurzer Bestrahlung bis 10^{-6} g bestimmen, bei langer Bestrahlung und Abkühlung bis 3.10^{-8} g, Tellur bis 10^{-6} g bei langer Bestrahlung und Abkühlung.

Résumé—On a étudié l'analyse par activation destructive et non destructive pour le sélénium et le tellurium. Dans l'analyse destructive, on co-extrait les activités du sélénium et du tellurium à partir des éléments irradiés et dissous de la gangue au moyen du réactif dithizone/CCl_4 dans une chambre chaude par manipulation à distance, puis les sépare l'une de l'autre par extraction au *N*,*N*-diéthyldithiocarbamate de diéthylammonium/CCl_4, le tellurium passant dans la phase organique et le sélénium étant retenu par la phase aqueuse. La sensibilité de la méthode est de 10^{-8} g pour les deux éléments. Par les méthodes non destructives, on peut doser le sélénium jusqu'à 10^{-6} g par courte irradiation et jusqu'à 3×10^{-8} g par longue irradiation et refroidissement, et le tellurium jusqu'à 10^{-6} g par longue irradiation et refroidissement.

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Determination of lanthanum by flame photometric titration

(*Received* 15 *January* 1968. *Accepted* 16 *April* 1968)

DETAILED studies have shown that in some flame photometric interferences there is a linear relationship between emission and the concentration of interferant, up to a limiting value of the latter, and no change in emission at higher concentrations of interferant. The limiting concentration usually corresponds to a simple stoichiometric compound formed from the two reactants. This may be called a stoichiometric interference, and has been studied by Fukushima[1] who tried to explain the nature of these apparently chemical reactions. Yofe and Finkelstein[2] even applied the laws of chemical equilibria to such phenomena, Erdey *et al.*[3] described a method for the determination of phosphate, based on the shift caused in the equilibrium by addition of a third reactant, and Erdey and Svehla[4] determined calcium by "flame photometric titration". Although not free from interferences, such a titration offers an increased selectivity because the wavelength of emission is characteristic of the emitting species. In a study of the flame photometry of lanthanum we found another stoichiometric interference and therefore examined the possibility of titration of lanthanum with phosphate.

EXPERIMENTAL

Solutions

Lanthanum chloride. Stock solution, 0·1*M*, prepared from lanthanum chloride heptahydrate and standardized complexometrically, and further diluted to 0·01*M*, 0·001*M* and 1000 ppm of La.

Diammonium hydrogen phosphate, 0·1*M*. Further diluted to 0·01*M* and 0·001*M*.

Zirconyl chloride, thorium chloride, cerium(III) chloride and aluminium chloride, 0·1*M*, Prepared from the hydrated salts. *Titanium(III) chloride*, 0·1*M*, prepared from commercial titanium chloride solution. *Yttrium chloride*, 0·1*M*, prepared by dissolving yttrium oxide in hydrochloric acid.

Apparatus

The Unicam SP 90 combined emission and absorption flame photometer was used with an acetylene–air flame. Recommended settings are, acetylene flow-rate 900 ml/min, air flow-rate 5 l./min, wavelength 560 mμ, slit-width 0·1 mm, burner height 2 cm, lowest damping.

Consumption of sample

The rate of consumption of solution under the conditions used is about 4·5 ml/min. The minimum time needed for full galvanometer response to a change in signal was 1 sec at the lowest damping setting (1). We read the maximum deflection after 1·2 sec. With 12 readings per titration the total consumption was about 1 ml, *i.e.*, 2% of the initial volume (50 ml). Since most of these readings were near the end-point the negative error was reduced because most of the solution had already been "titrated". If the titration is repeated with as few readings as possible before the end-point this error can be decreased considerably.

Interference by phosphate with lanthanum emission

The suppressing effect of phosphate on the flame emission of lanthanum was reported by Menis and Rains,[5] and Yofe *et al.*[6] but its stoichiometric nature was not pointed out. We prepared a set of 0·01*M* lanthanum solutions each containing 10 ml of hydrochloric acid (1 + 1) per 100 ml to prevent precipitation. Various amounts of phosphate were added and the solutions were diluted to final volume; the final phosphate concentration ranged up to 0·02*M*. The emission of each

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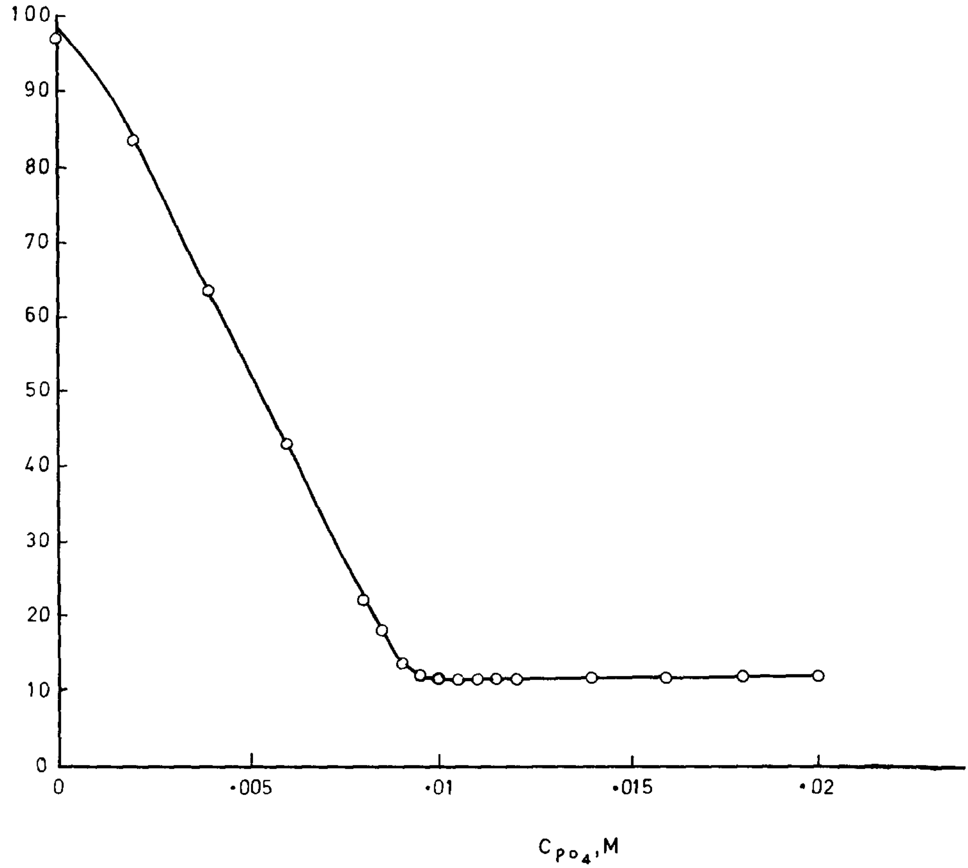

FIG. 1.—Variation of lanthanum emission at 560 mμ with phosphate concentration.

solution was measured at gain 5·4 and damping 2 and the readings were taken when steady. The results, plotted in Fig. 1, show a sharp intersection, termed the *stoichiometric point*, which corresponds to a 1:1 molar ratio between lanthanum and phosphate, indicating formation of $LaPO_4$. These conditions are suitable for a flame photometric titration.

Titration of lanthanum with phosphate

Because of the design of the instrument used we were obliged to remove the sample from it between additions of titrant but this did not cause much inconvenience. We added the titrant in suitable increments and took galvanometer readings after each addition. Titration curves obtained with 0·1 and 0·01*M* solutions are shown in Fig. 2.

The end-point is reached when there is no further change in the emission and can be determined quite easily without the titration curve being drawn. The results of titrations of 0·1, 0·01 and 0·001*M* lanthanum, shown in Table I together with those for "unknowns," indicate that accuracy and precision are both reasonable; the simplicity and rapidity offer advantages over other methods. The titration gives more precise results than the direct flame photometric determination of lanthanum, but reproducibility decreases considerably if 0·001*M* titrant is used.

At the start of the titration the gain has to be adjusted to yield a full-scale reading (90–100%). The readings near the end-point then become very low (say 10%) but can be increased by increasing the gain. The sensitivity is thus enhanced and the accuracy of end-point detection increased (Fig. 2).

Effect of foreign ions

We examined the effect of those metal ions which seriously interfere with the complexometric titration, namely cerium(III), yttrium, zirconium, titanium(III), thorium and aluminium, using them in about the same concentration as the lanthanum. Titrations with 0·1*M* titrant showed that cerium

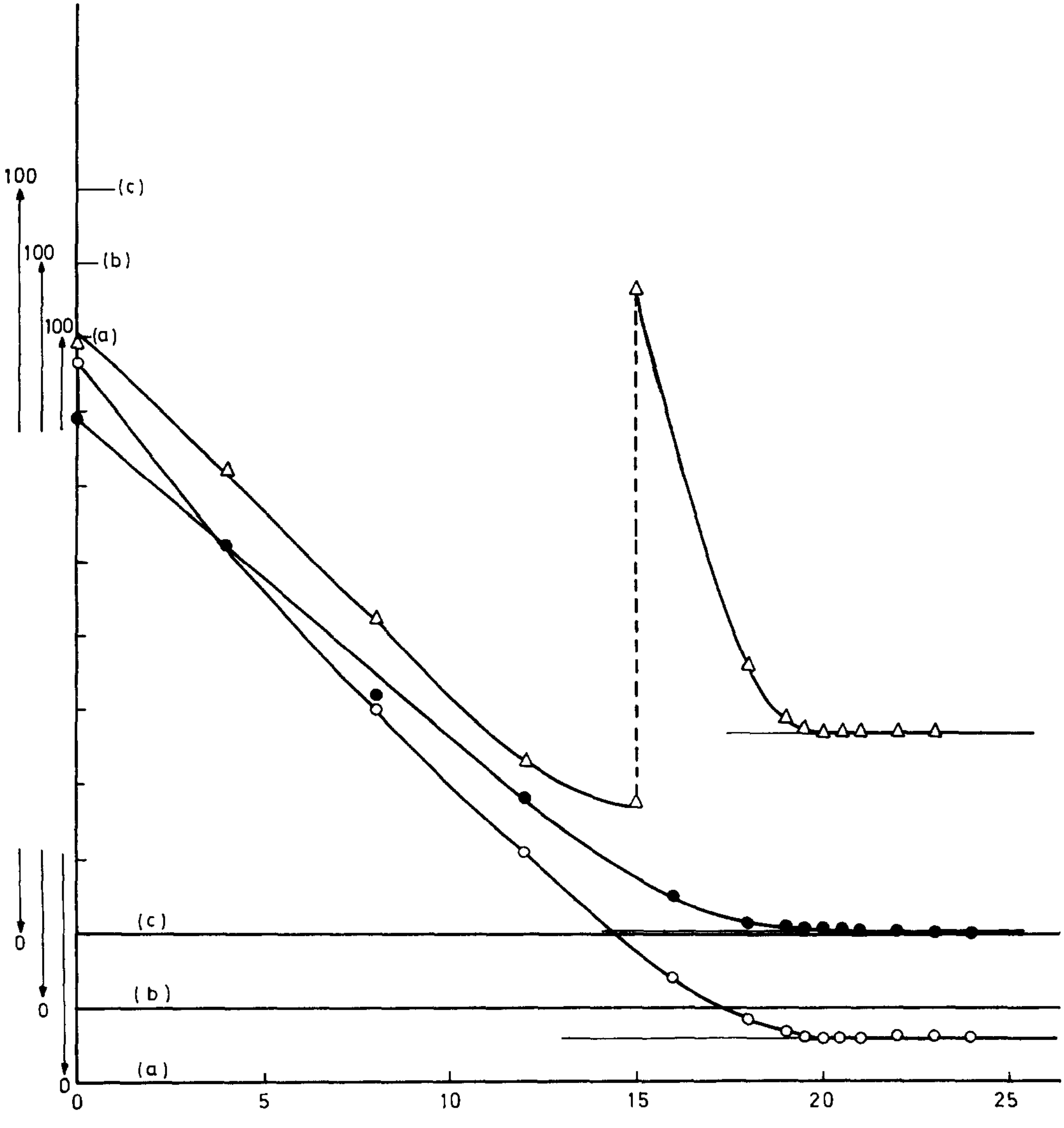

FIG. 2.—(*a*) ○—Flame photometric titration curve of 20·00 ml of 0·1*M* $LaCl_3$ titrated with 0·1*M* $(NH_4)_2HPO_4$. (*b*) ●—Flame photometric titration curve of 20·00 ml of 0·01*M* $LaCl_3$ titrated with 0·01*M* $(NH_4)_2HPO_4$. (*c*) △—Flame photometric titration curve of 20·00 ml of 0·1*M* $LaCl_3$ titrated with 0·1*M* $(NH_4)_2HPO_4$, increased sensitivity being used in the vicinity of the end-point.

TABLE I.—RESULTS OF FLAME PHOTOMETRIC TITRATION OF LANTHANUM

LaCl$_3$ solution taken		Titrant used			Std. devn.,
M	*ml*	*M*	*ml*		*ml*
0·1	20·00	0·1	20·0	19·6	0·3
			20·3	19·8	
			20·0	19·5	
	15·00		14·8	15·5	
			15·0		
	10·00		10·0	$10{\cdot}2_5$	
			10·0		
	5·00		5·0	$5{\cdot}1_5$	
			5·0		
0·01	20·00	0·01	20·0	19·0	0·6
			19·2	20·4	
			19·4	20·5	
	15·00		14·0	14·5	
			14·5		
	10·00		10·0	10·0	
			10·7		
	5·00		5·0	4·9	
			4·6		
0·001	20·00	0·001	19·0	18·0	
			19·5	21·4	
"*Unknowns*"					
0·1	17·5	0·1	17·4		
	8·3		8·0		
	8·2		7·8		
	15·6		15·5		
	6·7		7·0		
	14·3		14·1		

and yttrium (and presumably other tervalent rare earth metal ions) seriously interfere, but titanium(III) and zirconium show no interference at all. If thorium and aluminium are present the horizontal of the titration curve becomes oblique but is still a well-defined line: in that case, the end-point can only be determined reliably if the titration curve is plotted.

Procedure

Take a solution containing 70–300 mg of lanthanum, acidify it with 10 ml of hydrochloric acid (1 + 1) and dilute it with water to 50 ml. Titrate the solution with 0·1*M* diammonium hydrogen phosphate with constant stirring and take flame photometric emission readings from time to time, with the gain set to give initial full-scale deflection, until there is no further decrease in the emission readings. Determine the end-point graphically or from the readings themselves. If possible, carry out a second titration, adding about 80% of the titrant in one batch, before starting to take emission readings, with the gain set to give full-scale deflection at this point.

One ml of 0·1*M* diammonium hydrogen phosphate is equivalent to 13·9 mg of lanthanum.

Solutions containing 7–70 mg of lanthanum can be titrated in a similar way with 0·01*M* titrant but with reduced accuracy.

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Summary—The flame emission of lanthanum at 560 mμ decreases linearly with phosphate concentration until a 1:1 molar ratio is reached, and then remains practically constant. Lanthanum can be titrated with phosphate, the equivalence point being detected from the change in emission intensity. Errors due to consumption of solution by the atomizer can be kept low by using short spraying times and low galvanometer damping. The average error is about -1% for $0{\cdot}1M$ solutions and less than -5% for $0{\cdot}01M$. The method gives good results in the presence of titanium(III), zirconium, thorium and aluminium but cerium(III) and yttrium seriously interfere.

Zusammenfassung—Die Flammenemission von Lanthan bei 560 nm fällt linear mit der Phosphatkonzentration ab bis zum Molverhältnis 1 : 1 und bleibt dann praktisch konstant. Lanthan kann mit Phosphat titriert werden, wobei der Äquivalenzpunkt aus der Intensitätsänderung der Emission bestimmt wird. Fehler, die auf Lösungsverluste im Zerstäuber zurückgehen, lassen sich mit kurzen Sprühzeiten und geringer Dämpfung des Galvanometers klein halten. Der durchschnittliche Fehler ist bei $0{,}1M$ Lösungen etwa -1% und bei $0{,}01M$ Lösungen weniger als -5%. Die Methode liefert in Gegenwart von Titan(III), Zirkonium, Thorium und Aluminium einwandfreie Werte; Cer(III) und Yttrium stören dagegen beträchtlich.

Résumé—L'émission de flamme du lanthane à 560 mμ décroît linéairement avec la concentration en phosphate jusqu'à ce qu'un rapport molaire 1:1 soit atteint, puis reste pratiquement constante. On peut titrer le lanthane par le phosphate, le point d'équivalence étant détecté par le changement dans l'intensité d'émission. Les erreurs dûes à la consommation de solution par l'atomiseur peuvent être maintenues faibles en utilisant de courts temps de pulvérisation et un faible amortissement du galvanomètre. L'erreur moyenne est d'environ -1% pour des solutions $0{,}1M$ et de moins de -5% pour $0{,}01M$. La méthode donne de bons résultats en la présence de titane (III), zirconium, thorium et aluminium, mais le cérium (III) et l'yttrium interfèrent sérieusement.

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Improvement of the sensitivity of molybdenum and tungsten determination in niobium and tantalum*

(*Received* 6 *February* 1968. *Accepted* 13 *March* 1968)

In recent years, great strides have been made in producing refractory metals of extraordinary purity. In 1962, the dithiol method for determining molybdenum and tungsten in niobium was introduced[1,2] to cover the 50–1000 ppm range. Now, only five years later, commercially produced niobium frequently contains only a small fraction of the amounts of molybdenum and tungsten for which the method was designed. In addition, application of the method to the determination of

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* Work performed in part under Air Force Contract F33615-67-C-1524.

Summary—The flame emission of lanthanum at 560 mμ decreases linearly with phosphate concentration until a 1:1 molar ratio is reached, and then remains practically constant. Lanthanum can be titrated with phosphate, the equivalence point being detected from the change in emission intensity. Errors due to consumption of solution by the atomizer can be kept low by using short spraying times and low galvanometer damping. The average error is about −1% for 0·1*M* solutions and less than −5% for 0·01*M*. The method gives good results in the presence of titanium(III), zirconium, thorium and aluminium but cerium(III) and yttrium seriously interfere.

Zusammenfassung—Die Flammenemission von Lanthan bei 560 nm fällt linear mit der Phosphatkonzentration ab bis zum Molverhältnis 1 : 1 und bleibt dann praktisch konstant. Lanthan kann mit Phosphat titriert werden, wobei der Äquivalenzpunkt aus der Intensitätsänderung der Emission bestimmt wird. Fehler, die auf Lösungsverluste im Zerstäuber zurückgehen, lassen sich mit kurzen Sprühzeiten und geringer Dämpfung des Galvanometers klein halten. Der durchschnittliche Fehler ist bei 0,1*M* Lösungen etwa −1% und bei 0,01*M* Lösungen weniger als −5%. Die Methode liefert in Gegenwart von Titan(III), Zirkonium, Thorium und Aluminium einwandfreie Werte; Cer(III) und Yttrium stören dagegen beträchtlich.

Résumé—L'émission de flamme du lanthane à 560 mμ décroît linéairement avec la concentration en phosphate jusqu'à ce qu'un rapport molaire 1:1 soit atteint, puis reste pratiquement constante. On peut titrer le lanthane par le phosphate, le point d'équivalence étant détecté par le changement dans l'intensité d'émission. Les erreurs dûes à la consommation de solution par l'atomiseur peuvent être maintenues faibles en utilisant de courts temps de pulvérisation et un faible amortissement du galvanomètre. L'erreur moyenne est d'environ −1% pour des solutions 0,1*M* et de moins de −5% pour 0,01*M*. La méthode donne de bons résultats en la présence de titane (III), zirconium, thorium et aluminium, mais le cérium (III) et l'yttrium interfèrent sérieusement.

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In recent years, great strides have been made in producing refractory metals of extraordinary purity. In 1962, the dithiol method for determining molybdenum and tungsten in niobium was introduced[1,2] to cover the 50–1000 ppm range. Now, only five years later, commercially produced niobium frequently contains only a small fraction of the amounts of molybdenum and tungsten for which the method was designed. In addition, application of the method to the determination of

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molybdenum and tungsten in tantalum has been difficult because of excessive hydrolysis of tantalum during various stages of the procedure. For these reasons, it was found necessary to modify the method extensively to handle large sample weights of both niobium and tantalum.

EXPERIMENTAL

Reagents

Dithiol, 0·5% solution. Break a 5-g vial of reagent under the surface of 500 ml of 1*M* sodium hydroxide and stir till dissolved, heating to 35° if necessary. Add 10 ml of thioglycollic acid, dilute to 1 litre and store in 4-oz polythene bottles in the refrigerator.

Titanium(III) sulphate solution. Add 175 ml of water and 25 ml of conc. sulphuric acid to 1 g of titanium sponge in a 250-ml volumetric flask and heat in a boiling water-bath till dissolution is complete. Cool and dilute to volume. Prepare fresh before use.

Procedure

Weigh a sample of niobium or tantalum expected to contain 5–75 μg of molybdenum and or tungsten into a 200-ml Teflon beaker. Dissolve the sample in 25 ml of conc. hydrofluoric acid with dropwise addition of conc. nitric acid. Evaporate to a syrupy consistency on a steam-bath or under an infra-red lamp. Add 10 ml of conc. hydrofluoric acid and 5 ml of conc. hydrochloric acid and repeat the evaporation. If the amount of sample taken is 5 g or less, omit the procedure in the next paragraph.

Add the minimum amount of 4*M* hydrochloric acid–5*M* hydrofluoric acid ("acid mixture") required to obtain a clear solution after warming (a 10-g sample requires about 120 ml). Cool to below 25° and transfer to a polyethylene separatory-funnel containing 200 ml of isobutyl methyl ketone (IBMK), previously equilibrated with the acid mixture. Add a few drops of Methyl Orange (to aid in distinguishing the layers in the translucent funnel) and shake the funnel for at least 1 min. Drain the aqueous layer back into the original beaker. Wash the organic phase twice with 25 ml portions of the acid mixture, adding the washings to the original beaker. Evaporate to a syrupy consistency.

Add 10 ml of conc. sulphuric acid and 75 ml of the acid mixture to the syrupy solution obtained in either step above. Cover the beaker with a sheet of polyethylene held tightly in place with a rubber band and heat on a steam-bath until a clear solution is obtained. Remove the cover and add 0·1 g of hydroxylamine hydrochloride and 10 ml of dithiol reagent.[1,2] Heat for an additional 25 min, then cool to room temperature.

Add the sample solution to 10 ml of carbon tetrachloride already in a glass separatory-funnel and shake it for at least 1 min. Drain all but a few drops of the organic phase into a 25-ml volumetric flask. Wash the aqueous phase with two 7-ml portions of carbon tetrachloride, adding the washings to the flask. Drain the aqueous phase into the original Teflon beaker for the tungsten determination. Add a few crystals of anhydrous sodium sulphate to the volumetric flask and dilute to the mark with carbon tetrachloride. Measure the absorbance of the solution at 680 mμ in 2-cm cells against the solvent as reference. For amounts of molybdenum between 80 and 150 μg, 1-cm cells may be used. Calibrate over the range 5–80 μg of molybdenum by adding standard solution to beakers containing 75 ml of acid mixture and 10 ml of conc. sulphuric acid and developing the molybdenum dithiol colour as directed above.

Add 25 ml of 0·4% titanium(III) sulphate solution,[1,2] 70 ml of conc. hydrochloric acid and 10 ml of dithiol reagent[1,2] to the aqueous solution reserved for the tungsten determination. Heat for 30 min on a steam-bath, then cool to room temperature. Extract and measure as for molybdenum but at 640 mμ. Use 1-cm cells for $>$ 100 μg of tungsten. Calibrate over the range 5–80 μg of tungsten by adding standard solution to plastic beakers containing 75 ml of acid mixture, 10 ml of conc. sulphuric acid and 70 ml of conc. hydrochloric acid, adding titanium(III) and dithiol, and extracting.

DISCUSSION

Sensitivity

Because sample weights of 10 g or more can be used, the optimum range has been extended to as low as 0·5 ppm of molybdenum and/or tungsten in niobium. In addition, the hydrofluoric–hydrochloric acid medium permits analysis of tantalum for molybdenum and tungsten by the same method.

Preliminary removal of niobium or tantalum

We have found that a single extraction with isobutyl methyl ketone from the mixed acid medium will remove all but 500 mg of niobium or 100 mg of tantalum from 10 g of metal. Recoveries of molybdenum and tungsten are 98%. Although an increase in the hydrochloric acid concentration would result in a more complete removal of niobium, the loss of molybdenum would become significant. The amounts of niobium or tantalum remaining after a single extraction cause no interference in the suggested procedure.

Hydrofluoric acid–hydrochloric acid medium

More than 5 g of niobium or tantalum can be kept in solution with 75 ml of an acid mixture that is 4*M* in hydrochloric and 5*M* in hydrofluoric acid. After addition of sulphuric acid and dithiol reagent, the acid concentrations in the medium are H_2SO_4 1·9*M*, HCl 3·2*M* and HF 4·0*M*. The total acidity of this medium is 11·0*N*, very nearly the same as the 10·0*N* utilized in the earlier method for molybdenum determination. However, the relative proportions of the various acids are quite different. The dithiol complex of molybdenum is not formed as rapidly in the suggested medium but once formed it is more readily extracted. Thus with the 25-minute heating period recommended, as much as 5 mg of molybdenum can be extracted away from traces of tungsten. In the original medium, no heating was required but only about 0·5 mg of molybdenum could be extracted. The medium suggested for formation of the tungsten dithiol complex is 9·8*N* in total acidity, 1·1*M* H_2SO_4, 5·7*M* HCl and 1·9*M* HF. Again, the acidity is the same as in the earlier method but the proportions of the constituents have been altered to hold large samples of niobium and tantalum in solution. This change has no observable effect on the formation of the tungsten dithiol complex.

Effect of sulphuric acid

In the absence of sulphuric acid, 2 hr are required for full development of the molybdenum colour, and only 75% of the tungsten colour is developed after 3 hr. The need to add sulphuric acid may involve complexing of niobium and tantalum, since in the absence of these two elements, both the molybdenum and tungsten dithiol colours develop rapidly and completely even in the absence of sulphuric acid.

Effect of hydrochloric acid

Additional hydrochloric acid is required to provide a suitable medium for the formation of the tungsten–dithiol complex. Addition of 65 ml or more of the conc. acid ensures rapid and complete colour development; only 78% of the colour is obtained when 50 ml are added.

Determination of tungsten after molybdenum

In the original method[1,2] the aqueous phase remaining after the molybdenum determination was evaporated to fumes of sulphuric acid and treated with nitric acid to destroy residual organic matter. This step was time-consuming and troublesome, particularly when samples larger than the specified 150 mg were to be analysed. We have found that residual organic matter causes no difficulty in the tungsten determination and that the evaporation can be omitted.

Handling of hydrofluoric acid solutions in glass funnels

The simple expedient of adding the heavy solvent, carbon tetrachloride, to the funnel before addition of the sample solution effectively prevents hydrofluoric acid attack on the stop-cock. The same funnel may be used for several hundred determinations before attack of the stop-cock seat becomes noticeable.

RESULTS

The suggested method was applied to the determination of molybdenum and tungsten in samples of niobium and tantalum from the AGARD (Advisory Group for Aerospace Research and Development of NATO) programme. In addition, to cover a wider range, molybdenum and tungsten-free solutions of niobium were prepared by treating hydrochloric–hydrofluoric acid solutions of high-purity niobium with IBMK and stripping the niobium with water.

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TABLE I.—RESULTS OF ANALYSIS

Sample, *g*	Mo present, μg	Mo added, μg	Mo found, μg	W present μg	W added, μg	W found, μg
Nb 10*†	<1	20	19·8	<1	25	24·7
Nb 5*	<1	20	20·2	<1	25	25·2
Nb 5*	<1	60	61·2	<1	75	73·9
Nb 5	2	—	2·3	175	—	173·4
Nb 5	2	50	53·4	175	—	175·8
Nb 10†	4	—	3·7	350	—	‡
Nb 10†	4	50	55·2	350	—	‡
Nb 5	90	—	91·4	7000	—	‡
Ta 5	4	—	3·8	12·5	—	13·3
Ta 5	4	50	55·2	12·5	75	89·4
Ta 10†	8	—	7·5	25	—	26·3
Ta 10†	8	50	59·0	25	75	100·7

* Molybdenum and tungsten-free solutions of niobium were prepared by extracting 4*M* HCl–5*M* HF solutions of the sample with IBMK, and stripping with water. The solutions were then spiked with known amounts of molybdenum and/or tungsten.

† The bulk of the niobium or tantalum was removed by preliminary IBMK extraction, as described in the procedure.

‡ Tungsten not determined.

Summary—A more sensitive dithiol method is described for determination of as little as 0·5 ppm molybdenum and tungsten in high-purity niobium and tantalum. The increased sensitivity is achieved by taking a much larger sample and extracting the bulk of the Nb or Ta into isobutyl methyl ketone. Selective extraction then separates Mo and W.

Zusammenfassung—Eine empfindlichere Dithiolmethode zur Bestimmung von 0,5 ppm Molybdän und Wolfram in hochreinem Niob und Tantal wird beschrieben. Die erhöhte Empfindlichkeit wird erreicht durch Verwendung einer viel größeren Probe und Extraktion der Hauptmenge Niob oder Tantal in Isobutylmethylketon. Selektive Extraktion trennt dann Molybdän und Wolfram.

Résumé—On décrit une méthode dithiol plus sensible pour le dosage de quantités aussi petites que 0,5 p.p.m. de molybdène et de tungstène dans le niobium et le tantale de haute pureté. La sensibilité accrue est atteinte en prenant un échantillon beaucoup plus important et en extrayant la masse du Nb ou du Ta en méthylisobutylcétone. Une extraction sélective sépare alors Mo et W.

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Photometric determination of palladium with dimethylsulphonazo III

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ALMOST all known 3,6-bisarylazo derivatives of chromotropic acid (4,5-dihydroxy-2,7-naphthalenedisulphonic acid) give a very sensitive colour reaction with palladium(II).[1] Several of them have been recommended for photometric determination of this element.[2-4] Unfortunately these reactions are usually very unspecific so they are not very useful though this is not true of "Palladiazo".[3] The selectivity of their photometric reactions is modified advantageously by introduction of a suitable substituent into the *ortho* position (to the azo group) of the benzene ring. Of all the tested substituents (phosphonic, arsonic, stibonic, boronic, carboxyl, sulphonic, hydroxy, mercapto and aminomethyl groups), the sulphonic acid group appears the most favourable for the determination of palladium(II). The general photometric properties of a series of 3,6-bis(2-sulphophenylazo) derivatives of chromotropic acid have been reported recently.[5] Dimethylsulphonazo III, 3,6-bis (4-methyl-2-sulphophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid, appears to be the best of this group of reagents. Dimethylsulphonazo III reacts with palladium(II) in the range of acidity 0·01–0·2N (perchloric, hydrochloric or nitric acid) to give a complex with a molar absorptivity of $4{\cdot}0 \times 10^4$ at 620 mμ. Thorium, zirconium and hafnium interfere but can be masked by fluoride.

EXPERIMENTAL

Reagents

Dimethylsulphonazo III solution, $2{\cdot}00 \times 10^{-4}M$, was prepared by dissolution of 197 mg of the chromatographically pure ($R_F = 0{\cdot}38$; solvent system of 2M ammonia saturated with isobutanol) decahydrate of the tetrasodium salt in 1 litre of water. Ammonium fluoride and the nitrate or perchlorate salts of various metal ions (30 in all) were used as $10^{-3}M$ solutions.

Procedure

Add 7 ml of $10^{-3}M$ ammonium fluoride to a sample solution containing 0·01–0·40 μmole of palladium(II). Adjust the volume of solution to 20 ± 2 ml and the acidity to 0·0125–0·25N (perchloric, nitric or hydrochloric acid). Add 2·50 ml of $2{\cdot}00 \times 10^{-4}M$ dimethylsulphonazo III, mix, and dilute to 25·00 ml with water. Measure the absorbance against a reagent blank solution at 620 mμ in 1-cm cells.

RESULTS AND DISCUSSION

Examples of several practical determinations are given in Table I. Of the ions investigated, 10^{-3} μmole of zirconium, hafnium, chromium(III) and barium interfere. Lead(II), mercury(II), beryllium, thorium, vanadium(V), uranium (VI), bismuth, platinum(IV), molybdenum(VI), gold(III), and ruthenium(IV) interfere when present amounts of 5×10^{-3} μmole. Other ions in amounts up to 5 μmole do not interfere. Cyanide, EDTA, DCTA and DPTA interfere seriously in amounts above 2×10^{-4} μmole.

Palladium(II) forms a 1:1 complex with dimethylsulphonazo III (continuous variation and mole-ratio methods). The error of the method described does not exceed ± 5%.

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Summary—A sensitive and selective photometric determination of palladium(II) with dimethylsulphonazo III has been worked out. The effect of many other ions has been investigated.

Zusammenfassung—Eine selektive und empfindliche spektral photometrische Bestimmung von Palladium (II) mittels Dimethylsulfonazo III wurde ausgearbeitet. Der störende Einfluss von zahlreichen Ionen wurde untersucht.

Résumé—On a mis au point un dosage photométrique sensible et sélectif du palladium(II) au moyen de diméthylsulfonazo III. On a étudié l'influence de nombreux autres ions.

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Table I.—Determination of palladium(II)

Pd taken, *μmole*	Added, *μmole*		Pd found, *μmole*	Pd taken, *μmole*	Added, *μmole*		Pd found, *μmole*
0·020	—		0·020	0·100	Ge(IV)	1	0·101
0·100	—		0·099	0·100		5	0·103
0·200	—		0·201	0·100		10	0·104
0·300	—		0·301	0·100	Nb(V)*	1	0·099
0·400	—		0·399	0·100		5	0·100
0·100	Pb	0·001	0·099	0·100		10	0·104
0·100		0·003	0·102	0·300	Cd	1	0·301
0·100		0·005	0·107	0·300		10	0·305
0·200	Mn(II)	1	0·200	0·300		50	0·310
0·200		5	0·201	0·200	Zn	1	0·199
0·200		10	0·202	0·200		10	0·203
0·200	Be	0·001	0·199	0·200		50	0·207
0·200		0·003	0·205	0·100	KH_2PO_4	10^{-5}	0·099
0·200		0·005	0·212	0·100		0·1	0·102
0·200	La	1	0·201	0·100		1	0·104
0·200		5	0·205	0·100	Na-citrate	1	0·102
0·200		10	0·208	0·100		5	0·106
0·100	Hg(II)	0·001	0·099	0·100	In	1	0·101
0·100		0·003	0·103	0·100		5	0·102
0·100		0·005	0·107	0·100		10	0·103
0·100	Zr	10^{-4}	0·101	0·100	Ca	1	0·100
0·100		5×10^{-4}	0·103	0·100		5	0·102
0·100		0·001	0·106	0·100		10	0·106
0·200	Th	0·001	0·203	0·100	Pt(IV)‡	0·001	0·099
0·200		0·003	0·207	0·100		0·003	0·103
0·200		0·005	0·212	0·100		0·005	0·107
0·100	V(V)†	0·001	0·102	0·200	Mo(VI)¶	0·001	0·202
0·100		0·003	0·104	0·200		0·003	0·207
0·100		0·005	0·107	0·200		0·005	0·212
0·200	U(VI)	0·001	0·199	0·100	Au(III)‡	0·001	0·099
0·200		0·003	0·205	0·100		0·003	0·103
0·200		0·005	0·212	0·100		0·005	0·107
0·100	Bi	0·001	0·099	0·200	Fe(III)	1	0·201
0·100		0·003	0·103	0·200		3	0·205
0·100		0·005	0·107	0·200		5	0·207
0·200	Ba	10^{-4}	0·202	0·200	Cr(III)	10^{-4}	0·206
0·200		5×10^{-4}	0·208	0·200		0·001	0·185
0·200		10^{-3}	0·213	0·200		0·010	0·167
0·100	Co(II)	1	0·101	0·200	K_2SO_4	0·1	0·201
0·100		5	0·103	0·200		1	0·204
0·100		10	0·104	0·200		5	0·200
0·200	Ni	1	0·202	0·200	$Na_2C_2O_4$	1	0·198
0·200		5	0·202	0·200		3	0·195
0·200		10	0·205	0·200		5	0·197
0·100	Al	1	0·101	0·100	$C_4H_5O_6K$	0·1	0·097
0·100		5	0·102	0·100		1	0·095
0·100		10	0·102	0·100		5	0·092
0·200	Cu(II)	1	0·203	0·100	EDTA	10^{-5}	0·099
0·200		3	0·204	0·100		10^{-4}	0·097
0·200		5	0·208	0·100		2×10^{-4}	0·094
0·100	Mg	1	0·099	0·100	DCTA	10^{-5}	0·101
0·100		10	0·102	0·100		10^{-4}	0·096
0·100		100	0·103	0·100		2×10^{-4}	0·092
0·300	Ru(IV)	0·001	0·303	0·100	DPTA	10^{-5}	0·098
0·300		0·003	0·309	0·100		10^{-4}	0·097
0·300		0·005	0·318	0·100		2×10^{-4}	0·093
0·200	Sr	1	0·200	0·100	KCN	10^{-5}	0·097
0·200		3	0·206	0·100		10^{-4}	0·096
0·200		5	0·209	0·100		2×10^{-4}	0·093

* Potassium metaniobate. † Ammonium metavanadate. ‡ Chloride. ¶ Ammonium molybdate.

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Extractive photometric determination of cobalt with Acid Monochrome Green S

(*Received* 9 *November* 1967. *Accepted* 26 *February* 1968)

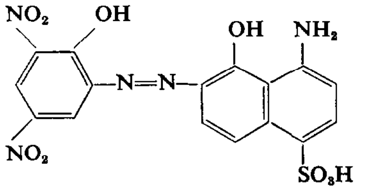
In an earlier general study[1,2] it was found that butanol extracts from neutral or weakly alkaline solution the complex of cobalt with Acid Monochrome Green S. This extraction procedure has now been developed into a quantitative method for cobalt determination.

EXPERIMENTAL

Reagents

Cobalt(II) chloride solution. $3{\cdot}4 \times 10^{-4}M$.

Acid Monochrome Green S, 0·2% *aqueous solution*. The purity of the reagent was checked by paper chromatography with chloroform-ethanol (1:1); a single spot was obtained (viewed in visible and ultraviolet light).



Acid
Monochrome
Green S
(C.I.17125)

Sodium chloride, 4*M*. Prepared in the borate buffer used for pH regulation (0·1*M* hydrochloric acid and 0·05*M* borax for pH 7–9·2; 0·1*M* sodium hydroxide and 0·05*M* borax for pH 9·3–12·4; for pH 10,600 ml of borax solution and 400 ml of sodium hydroxide solution).

Analytical grade reagents were used whenever possible.

Procedure

Dyestuff solution (0·75 ml) was added to cobalt solution (0·75 ml) tagged with ^{60}Co tracer and the mixture was diluted to 5 ml with pH 10 buffer. The initial reagent concentrations were cobalt $5{\cdot}1 \times 10^{-5}M$, dyestuff $6{\cdot}4 \times 10^{-4}M$. The solution was shaken for 30 sec with 5 ml of butanol in a test-tube with a ground-in stopper, the phases were allowed to separate, and then 3 ml of each phase were withdrawn into glass test-tubes and the activity was measured in a scintillation counter with an NaI(Tl) crystal. The experiment was repeated with various amounts of sodium chloride added as a solution in the buffer used. The distribution coefficient *E* and the degree of extraction *R* were calculated. Photometric measurements were made in 1-cm cells, and the pH of the aqueous phase at equilibrium was measured with a pH meter.

RESULTS

The degree of extraction was found to be maximal at pH 9·5–11·5, and the pH was therefore kept at 10 for further studies. The equilibrium pH was not significantly different from the initial pH. The extraction was enhanced by the presence of sodium chloride (for discussion of influence of neutral salts on chelate extraction see Zolotov *et al.*[3]), cobalt being almost completely extracted (98–99%) in one extraction when the sodium chloride concentration exceeded 1·5*M*, but only 70% extracted in the absence of the salt. In the presence of sodium chloride the degree of extraction was constant when the

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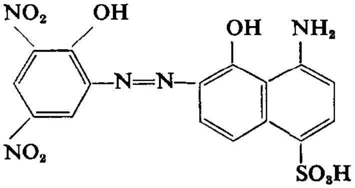
EXPERIMENTAL

Reagents

Cobalt(II) chloride solution. 3·4 × $10^{-4}M$.

Acid Monochrome Green S, 0·2% *aqueous solution.* The purity of the reagent was checked by paper chromatography with chloroform-ethanol (1:1); a single spot was obtained (viewed in visible and ultraviolet light).



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Analytical grade reagents were used whenever possible.

Procedure

Dyestuff solution (0·75 ml) was added to cobalt solution (0·75 ml) tagged with ^{60}Co tracer and the mixture was diluted to 5 ml with pH 10 buffer. The initial reagent concentrations were cobalt 5·1 × $10^{-5}M$, dyestuff 6·4 × $10^{-4}M$. The solution was shaken for 30 sec with 5 ml of butanol in a test-tube with a ground-in stopper, the phases were allowed to separate, and then 3 ml of each phase were withdrawn into glass test-tubes and the activity was measured in a scintillation counter with an NaI(Tl) crystal. The experiment was repeated with various amounts of sodium chloride added as a solution in the buffer used. The distribution coefficient *E* and the degree of extraction *R* were calculated. Photometric measurements were made in 1-cm cells, and the pH of the aqueous phase at equilibrium was measured with a pH meter.

RESULTS

The degree of extraction was found to be maximal at pH 9·5–11·5, and the pH was therefore kept at 10 for further studies. The equilibrium pH was not significantly different from the initial pH. The extraction was enhanced by the presence of sodium chloride (for discussion of influence of neutral salts on chelate extraction see Zolotov *et al.*[3]), cobalt being almost completely extracted (98–99%) in one extraction when the sodium chloride concentration exceeded 1·5*M*, but only 70% extracted in the absence of the salt. In the presence of sodium chloride the degree of extraction was constant when the dyestuff:cobalt ratio exceeded 10 (see Fig. 1). The sodium chloride concentration was kept constant at 1·6*M* for further work.

The radiometric experiments showed that the extraction is practically instantaneous, there being no change in the degree of extraction when the shaking-time was varied from 30 sec to 1 hr. On the other hand, the absorbance of the extract (measured against a reagent blank obtained with 30-sec extraction) increased with increase in shaking-time, becoming constant only for shaking-times longer than 30 min. We attribute this to slow extraction of the excess of reagent (which also absorbs at the wavelength used for the measurements). A shaking-time of 30 sec was therefore selected as standard practice, because the cobalt extraction was maximal and the reagent extraction was minimized.

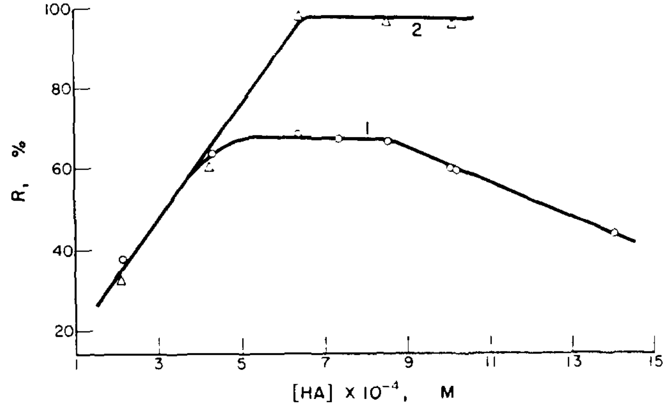

FIG. 1.—Dependence of cobalt extraction on concentration of the reagent. *1*—No NaCl; *2*—in presence of 2*M* NaCl. Cobalt 5·1 × $10^{-5}M$

The absorption spectra of the dyestuff and the complex are shown in Fig. 2. The reagent has λ_{max} at 585 mμ, and the complex at 625 mμ. The sodium chloride has little effect on the absorption spectrum of the complex. Measurements should be made at 625 mμ or with a light-filter with maximum transmittance at this wavelength. The photometric measurements confirmed that the initial dyestuff: cobalt ratio should exceed 10 for complete extraction. With 4·2 × $10^{-4}M$ dyestuff initially present, Beer's law is obeyed for cobalt concentrations of 0·02–2 μg/ml, but not for concentrations above 2 μg/ml. The molar absorptivity of the complex is 3·2 × 10^4.

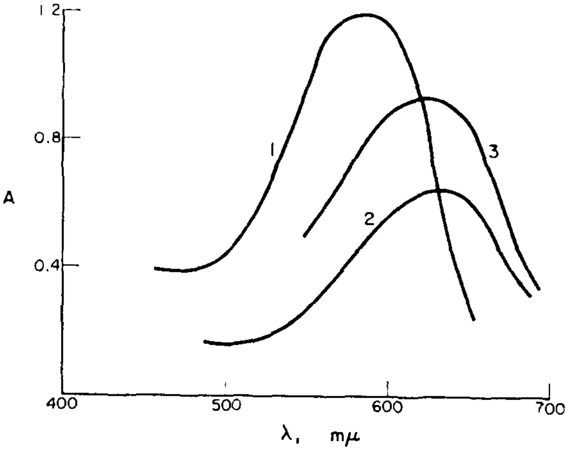

FIG. 2.—Absorption spectra of the reagent and the complex in butanol. *1*—Reagent; *2*—complex; *3*—complex extracted in presence of 2*M* NaCl. Cobalt $10^{-5}M$; reagent 1·3 × $10^{-4}M$

Citrate and fluoride do not interfere in amounts up to 10000 times that of the cobalt, nor does tartrate in 5000-fold excess, but EDTA interferes severely and must be absent. Citrate or tartrate was therefore added to prevent hydrolysis of cations. The relative error in cobalt determination was less than 7% in the presence of 1000-fold amounts of Ga, Th and Ca, 100-fold amounts of rare earths, Sc, Al and Pb, 10-fold amounts of Zn, U and Ti, and equal amounts of Cu and Fe(III), though the iron can be masked with fluoride. Nickel interferes at all levels, presumably by forming a similar extractable complex.

The sensitivity of the reaction is high, and compares favourably with that of other methods for cobalt (Table I). The reagent solution is stable, the colour of the complex is stable (for at least 24 hr), and the reproducibility is good. The method was used to determine 1–50 × 10^{-5}% of cobalt in gallium metal, with a relative error of 10%.

TABLE I.—SENSITIVITY OF PHOTOMETRIC METHODS OF DETERMINING COBALT[4]

Reagent	Solvent	Molar absorptivity
Acid Monochrome Green S	Butanol	32000
1-Nitroso-2-naphthol	Chloroform	26500
2-Nitroso-1-naphthol	Water	15000–25000
Thiocyanate	Cyclohexanol	20000
Nitroso-R-salt	Water	15000
Thiocyanate	Isoamyl alcohol	6000
Thiocyanate + tetraphenylarsonium	Chloroform	1500
Diethyldithiocarbamate	Carbon tetrachloride	1400

Determination of cobalt in gallium metal

Dissolve 1 g of sample in *aqua regia* with moderate heating, evaporate the solution to a syrup, take it up in 10 ml of 8·5*M* hydrochloric acid. Extract the bulk of the gallium with three 10-ml portions of di-isopropyl ether, back-washing each extract with 5 ml of 7*M* hydrochloric acid (cobalt has a distribution coefficient of 0·1 under the conditions used). Combine the aqueous phases and evaporate them almost to dryness. Take up in 1·5 ml of water, add 0·5 ml of 2·5% sodium fluoride solution as masking agent, 0·5 ml of 5% sodium citrate solution, 0·5 ml of 0·2% dyestuff solution and 2 ml of 4*M* sodium chloride in pH 10 borate buffer, and extract with 5 ml of butanol for 30 sec in a 20-ml separating funnel. Measure the absorbance of the organic phase at 625 mμ. Use the standard addition method for calibration—dissolve 1-g samples and add 2 and 5 μg of cobalt (in solution) and then carry these standards through the procedure.

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Summary—Cobalt forms with Acid Monochrome Green S a complex which can be extracted quantitatively into butanol from 1·6*M* sodium chloride medium at pH 9·5–11·5. The molar absorptivity of the complex is 3·2 × 10^4 at 625 mμ. The method has been used to determine cobalt in gallium metal.

Zusammenfassung—Kobalt bildet mit saurem Monochromgrün S einen Komplex, der aus einer Medium mit 1,6 M Natriumchlorid und pH 9,5–11,5 quantitativ in Butanol extrahiert werden kann. Der molare Extinktionskoeffizient des Komplexes ist 3,5 × 10^4 bei 625 nm. Die Methode wurde zur Bestimmung von Kobalt in metallischem Gallium verwendet.

Résumé—Le cobalt forme avec le Vert Monochrome Acide S un complexe que l'on peut extraire quantitativement en butanol à partir d'un milieu à pH 9,5–11,5, 1,6 *M* en chlorure de sodium. Le coefficient d'absorption moléculaire du complexe est de 3,2 × 10^4 à 625 mμ. On a utilisé la méthode pour doser le cobalt dans le gallium métallique.

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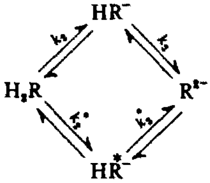
ANNOTATION

Metal complexes of PAR, TAR and PAN

In recent years, PAR, TAR and PAN have received considerable attention as analytical reagents. In studies with PAR and TAR, it has been recognized[1–6] that a difficulty exists in determining metal-complex formation constants because of uncertainty associated with the choice of the p*k* value for the *o*-hydroxy group. Chalmers[6] has recently presented the relevant acid-dissociation equilibria diagrammatically and his notation system is used below. The microscopic dissociation pathways[7] can be written as follows (the pyridinium dissociations, k_1 and k_1^*, have been ignored):



k_2 = *p*-OH group
k_3 = *o*-OH group
k_2^* = *o*-OH group
k_3^* = *p*-OH group

Implicit in previous work is the assumption that $k_2 \gg k_2^*$ and $k_3^* \gg k_3$, so that k_2 and k_3 are essentially equal to the macroscopic constants and have been taken as such. Selected macroscopic constants for PAR, TAR and the related compounds, PAN and TAMR [5-methoxy-2(2-thiazolylazo)-phenol], are listed in the table.

Table I.—Macroscopic p*k* values for PAR, TAR and related compounds

Compound	pk_2	pk_3	Solvent	Reference
PAR	6·87	13·42	50% dioxan–H_2O	2
	7·01	13·00	50% dioxan–H_2O	8
	6·9	12·4	50% dioxan–H_2O	1
TAR	7·37	12·80	50% dioxan–H_2O	2
	6·23	9·44	H_2O	9
PAN	12·3	—	50% dioxan–H_2O	1
	12·2	—	20% dioxan–H_2O	10
TAMR	6·70	—	H_2O	11
	7·08	—	H_2O	12

For the metal complexes of PAR and TAR, the chelating species has conventionally been taken to be HR^{*-}, requiring that k_2^* be known for the calculation of formation constants. Past workers[1–4,13,14] have used k_3 as an approximation to k_2^*. For the PAR complexes, this assumption was justified on the basis that the dissociation of the *p*-OH group appeared to have little effect on the dissociation of the *o*-OH group, since k_3 for PAR was essentially equal to k_2 for PAN.[1] In view, however, of higher k_3 values in the literature (see Table), this assumption may not be valid. A re-examination of the k_3 value for PAR should be made.

Chalmers[6] has stated that the use of k_2 is preferable to k_3 since the difference between pk_3 and pk_2 (about 5–6 units) is due almost entirely to the inductive effect of the dissociated *p*-OH group and only in small part to hydrogen bonding.† In resorcinol, however, the difference is only 1·80 units (pk_1 = 9·29, pk_2 = 11·09, in water; p$k_1 \sim 11$, p$k_2 \sim 13$, in 50% dioxan–water, at 25°[15]),

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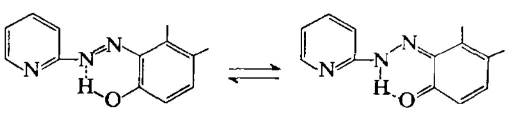
† Others[1] have attributed the high pk_3 value mainly to hydrogen bonding; however, it is now well known that hydrogen bonding causes a decrease in p*k*, not an increase. Therefore, it is best to explain the relative magnitudes of pk_2 and pk_3 on the basis that the pk_2 value is abnormally low (due to the strong electron-withdrawing effect of the pyridylazo system) and the pk_3 value is essentially normal (*e.g.*, compare with resorcinol).

so that the large difference above must be due mainly to the effect of the pyridylazo system on pk_2. The use of k_2 for k_2^*, then, would be too severe an approximation and it appears, as also suggested by Chalmers, that the most reliable value of k_2^* would be obtained by determining the dissociation constant of the *o*-OH group in the *p*-methoxy derivatives of PAR and TAR. This procedure, incidentally, would also yield the value of k_3^*, through the relationship $k_2/k_2^* = k_3^*/k_3$.[7]

Two additional points of interest arise in connection with reagents such as PAR, TAR and PAN. First, although the value p$k \sim 13$ has been ascribed to the pure *o*-OH dissociation, there is little evidence to rule out the complicating tautomeric equilibrium:



Appreciable formation of the hydrazone tautomer would necessitate correction of the reported *o*-OH pk values (and of the corresponding formation constants). In related compounds such as substituted *o*-hydroxyazobenzenes and *o*-hydroxyazonaphthols, infrared studies have shown the existence of strong hydrogen bonding and tautomeric forms.[16-20] Hadži[19] and Snavely[20] have reported, however, that only the azonaphthols form an appreciable amount of the hydrazone form. This observation implies that hydrazone formation would perhaps be an important factor with PAN but not with PAR and TAR. A re-investigation of these systems should be made. Secondly, in written equilibria, the reactive ligand species is shown to be anionic but this is purely conventional and is not supported by experimental evidence. Indeed, it is highly likely that the reactive species is the neutral ligand, since in general, complex formation occurs in acid solution and the concentration of the neutral species could be 10^8–10^{12} times that of the anionic species, *i.e.*, sufficient to compensate for rate-constant effects. When the possibility of tautomer existence is additionally considered, it is clear that our knowledge of these systems is at best preliminary.

Acknowledgement—The author is grateful to Mr. H. Steger for help rendered on this problem.

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Summary—A discussion of the problem of assignment of a pk value for the hypothetical dissociation of the *o*-OH proton in TAR, PAR and PAN before the *p*-OH proton. The view is expressed that the most reasonable choice is to use the normal pk value for this dissociation, rather than the normal pk value for the *p*-OH proton.

Résumé—Une discussion du problème de l'attribution d'une valeur pk pour la dissociation hypothétique du proton *o*-OH dans TAR, PAR et PAN avant le proton *p*-OH. On exprime l'idée que le choix le plus raisonnable est d'utiliser la valeur de pk normale pour cette dissociation, plutôt que la valeur de pk normale pour le proton *p*-OH.

Zusammenfassung—Eine Diskussion des Problems der Zuordnung eines pK-Wertes zur hypothetischen Dissoziation des *o*–OH-Protons in TAR, PAR und PAN vor dem *p*–OH-Proton. Es wird die Ansicht vertreten, daß man am vernünftigsten den normalen pK-Wert dieser Dissoziation wählt, besser als den normalen pK-Wert des *p*–OH-Protons.

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SPECTROSCOPY IN SEPARATED FLAMES—IV

APPLICATION OF THE NITROGEN-SEPARATED AIR–ACETYLENE FLAME IN FLAME-EMISSION AND ATOMIC-FLUORESCENCE SPECTROSCOPY

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Summary—The primary and secondary combination zones of an air–acetylene flame have been separated by a stream of nitrogen flowing parallel to the flame to prevent access of atmospheric oxygen to its base. The flame is very stable over a wide range of fuel–air mixture strengths, and organic solvents may be aspirated without difficulty. The low flame background enables thermal-emission and atomic-fluorescence measurements to be made with high sensitivity. Bismuth, for example, has been determined in the range 5–200 ppm by its thermal emission at 306·8 nm, with a detection limit of 2 ppm in aqueous solution, and in the range 1–10 ppm with a detection limit of 0·3 ppm in 50% ethanolic solution. Zinc and cadmium have been determined at 213·9 nm and 228·8 nm by atomic-fluorescence spectroscopy in this flame with detection limits of 2×10^{-4} ppm and 5×10^{-4} ppm respectively, vapour-discharge lamps being used as sources of excitation. The results obtained represent a considerable improvement over those available by the same methods in a conventional air–acetylene flame.

In a previous communication from this laboratory we reported an investigation of the utility of the separated air–acetylene flame in thermal emission spectroscopy.[1] The secondary diffusion zone was separated by using a silica tube, and the atomic emission in the interconal zone for aspirated metal ion solutions was viewed through the tube. This use of the separated flame produced a considerable increase in the analytical-signal-to-flame-background ratio by depression of the latter to a very marked extent.

This communication describes some results obtained by separation of the air–acetylene flame without the use of a silica separator tube. In the burner described here, nitrogen is driven upwards in a laminar flow around the premixed laminar flame produced at a commercially available cylindrical burner, and "lifts-off" the secondary diffusion zone by preventing the access of atmospheric oxygen to support a diffusion zone in the lower parts of the flame. A similar type of flame has recently been used by Zeegers and Alkemade to study radical recombination reactions in air–acetylene flames.[2] This alternative method of separating the flame possesses the same advantages as the arrangement described earlier,[1] *i.e.*, the interconal zone exhibits low radiative background, so that greatly improved analytical-signal-to-flame-background ratios are obtained for aspirated metal ion solutions. It has several very clear advantages over the silica separator arrangement, however. Thus a wide range of fuel–air mixture strengths can be employed, and a wide range of organic solvents may safely be aspirated into the flame. In addition it is not necessary to view the analytical emission through the silica separator tube. The burner assembly used is simple to construct, safe to operate and easily supports stable "separated" flames. Some results are presented for the determination of bismuth by thermal emission spectroscopy, for which the separated air-acetylene flame is particularly suitable, and for the determination of cadmium and zinc by atomic-fluorescence spectroscopy.

EXPERIMENTAL

Apparatus

The burner and sheathing arrangement used in this study are shown in Fig. 1. A conventional cylindrical Unicam SP900 air-acetylene emission burner was employed. This was held centrally within a brass tube (4 cm in diameter) by a large rubber bung. The upper end of the brass tube lay in the same horizontal plane as the burner head. Nitrogen (oxygen-free grade) was supplied to this sheathing tube through four copper tubes spaced equally around the bung and supplied *via* a manifold arrangement from a rotameter (2–20 l./min) connected to a nitrogen cylinder. (For clarity only two of the nitrogen inlet tubes are shown in Fig. 1.) The nitrogen stream from this sheathing tube was made laminar at the exit of the tube by passage through a tightly wound spiral of alternate corrugated and flat stainless-steel strips (0·1 mm thickness, 2 cm wide) positioned *ca.* 2·5 mm below the burner head plate. The nitrogen flow-rate required to support a stable "lifted-off" secondary diffusion zone varies somewhat with the flame mixture strength and tightness of packing of the stainless steel strips. We have found, however, that stable separated flames can be obtained over a wide range of acetylene-air mixture strengths when the nitrogen flow-rate is maintained at *ca.* 10 l./min.

Air and acetylene pressures and flow-rates were controlled by the gas control unit on the Unicam SP900A flame spectrophotometer, which was used for the quantitative measurement of radiation from the flame. The spectrophotometer was fitted with an EMI 9601B photomultiplier tube. Thus the burner arrangement employed replaced the conventional burner unit fitted to the commercial flame photometer equipment. The samples were introduced as aqueous or 50% ethanolic solutions of their salts, *via* the Unicam indirect nebulizer operating on air.

Atomic-fluorescence measurements

The experimental arrangement employed for the atomic-fluorescence studies was similar to that described by Dagnall, West and co-workers[3,8]; 20-W Wotan zinc and cadmium vapour discharge lamps, operated at 1·5 A and 50 Hz from a ballast unit, were employed for excitation of fluorescence. The outer glass envelopes of these lamps were removed to permit transmission of the ultraviolet radiation, and the lamps were carefully shielded from draughts. The shielded flame burner and monochromator/detector arrangement was identical to that used for the thermal emission studies. The SP900A spectrophotometer was used in the emission mode, *i.e.*, the radiation from the flame was chopped at 100 Hz to match the *a.c.* amplifying frequency. The discharge lamp sources were mounted 7·5 cm from the flame, opposite to the atomic-absorption attachment, so that with the entrance slit of the spectrophotometer they subtended a right angle to the centre of the flame.

RESULTS AND DISCUSSION

In contrast to the conventional air–acetylene flame, the hottest part of the nitrogen-separated flame immediately above the primary reaction zone exhibits very low radiative background because of the absence of secondary combustion reactions. Atomic emission of analytical interest in this zone may, therefore, be viewed without interference from the background radiation of a secondary flame zone. We have thus found that the background emissions from OH and the CO + O continuum, almost all of which originate in the secondary zone, are at least two orders of magnitude lower in the interconal zone of the nitrogen-separated flame than in the conventional flame. The background emission spectrum from the nitrogen-separated flame appears almost identical to that reported earlier for the mechanically separated flame.[1] Also, as we have reported for the silica separator burner arrangement, the effective flame temperature immediately above the primary zone of the nitrogen separated flame may be shown to be lower in the shielded flame than in an ordinary air–acetylene flame. Results obtained with the two-line method of temperature measurement indicate that for iron in this region of the flame there is an electronic excitation temperature of

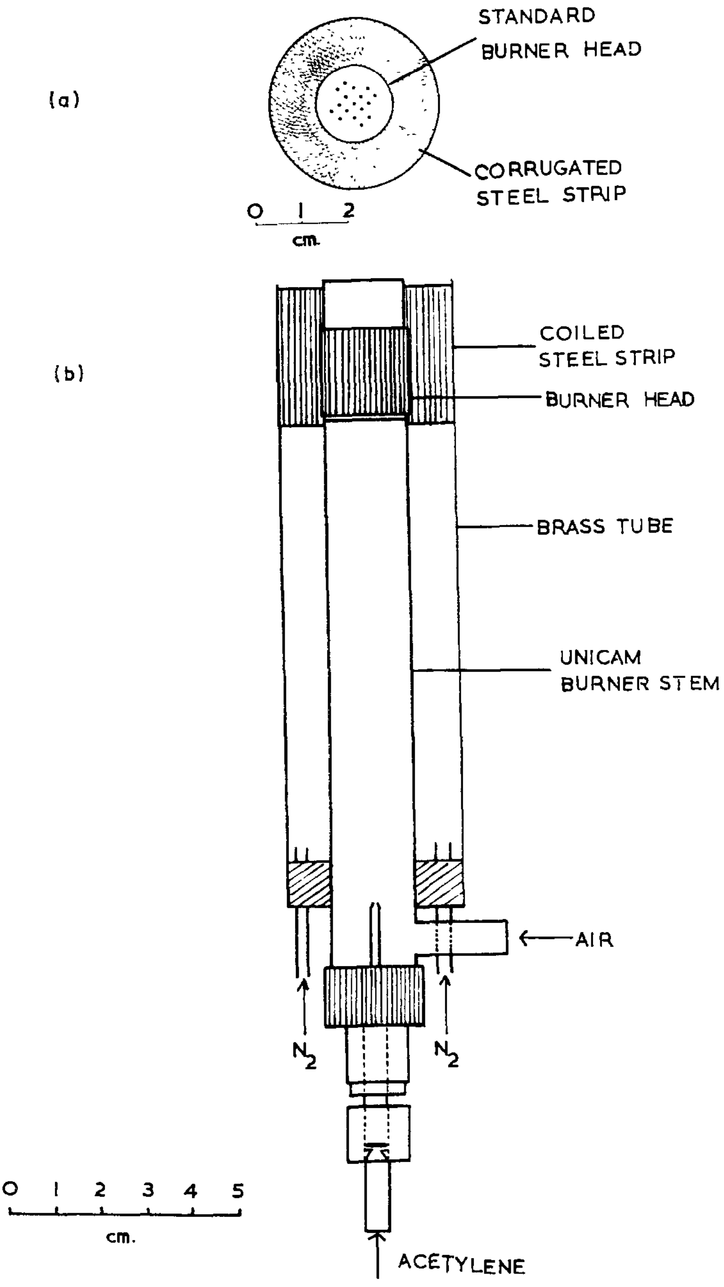

FIG. 1.—Burner arrangement for nitrogen-separated air–acetylene flame.

2420 ± 20°K in the conventional flame and 2320 ± 20°K in the nitrogen-separated flame. The loss of absolute intensity which arises from this small drop in temperature when the secondary zone no longer surrounds the hottest zone is more than compensated for analytically by the very great increase in the analytical-signal-to-flame-background ratios, and stability of the signals obtained over most of the near-ultraviolet and visible spectrum.

In order to demonstrate the practical utility and advantages of this separated air–acetylene flame, we have made a study of the determination of bismuth by thermal emission and zinc and cadmium by atomic-fluorescence spectroscopy, utilizing this flame and a conventional air–acetylene flame supported at the same burner. The experimental arrangement employed for the study of each flame was identical, so that the change from the conventional flame to the separated flame was made by simple control of the nitrogen flow-rate.

Effect of organic solvents

The increase in sensitivity which can usually be obtained in flame photometry when samples are nebulized in an organic solvent medium is well known. When the air–acetylene flame is separated with a silica separator tube, some difficulty is encountered when organic solvents are introduced into the flame. With many solvents it is difficult to maintain a stable separated flame, and some organic solvents give rise to deposition of carbon on the silica tube. With the nitrogen-separated flame, however, a wide range of organic solvents may be nebulized without difficulty. Thus stable separated flames were obtained when ethanol, n-butanol, isobutyl acetate, ethyl acetate, isobutyl methyl ketone, amyl alcohol, acetylacetone, acetic acid and isopropanol were nebulized into the nitrogen-separated flame. The problem of "sooting-up" does not arise with this flame as it does with the silica separator.

Determination of bismuth

Bismuth may be determined by its thermal emission at several atomic lines in a variety of flames. By far the strongest line is the resonance line at 306·8 nm ($^4S_{1\frac{1}{2}}$ — $^4P_{0\frac{1}{2}}$), but in most conventional flames the background in this region from the OH band head at 306·4 nm obscures the atomic emission and reduces the sensitivity of the bismuth determination. This problem does not arise with the oxy-cyanogen flame, and a detection limit of 3 ppm for bismuth has been reported.[4] However, with the flames more generally used for atomic-emission spectroscopy, *e.g.*, air or oxy-hydrogen and air or oxy-acetylene, bismuth is usually determined at an emission line other than that at 306·8 nm because of interference from the OH band. Dean and Carnes[5] used organic solvents in conjunction with a special light guide and reported detection limits of 6·4 ppm at 223·1 nm in the primary reaction zone of an oxy-acetylene flame and 2·8 ppm at 289·8 nm in an air-hydrogen flame. With the burner and detector system described here, the emission from bismuth at 306·8 nm is easily observed against the low OH flame background radiation, allowing greatly improved detection limits with low slitwidths and a detection system of only moderate sensitivity and resolution.

Height of observation in the flame

It is well known that the flame temperature falls with increasing height above the burner-head in premixed air-supported hydrocarbon flames, and that because the intensity of atomic emission in the flame varies exponentially with its temperature, there is a rapid fall in the intensity of atomic lines as the height of observation in the flame is increased. For this reason, much of the earlier work on the flame photometric determination of bismuth has made use of the primary reaction zone of the flame to obtain the maximum sensitivity. In the separated flame the emission intensity decreases even more rapidly with height, owing to the absence of the surrounding hot diffusion zone. However, it has been found that the maximum benefit from separating the flame is derived immediately above the primary zone, since the reduction of flame background is many times greater in the interconal zone than in the primary zone of the flame. Further, the variation of emission intensity with height in the separated flame at different fuel strengths appears to be identical with that reported earlier for the silica tube separated flame,[1] *i.e.*, the position of maximum emission is relatively independent of the mixture strength and occurs just above the primary zone. In view of this, all the work described here was carried out with the level of the bottom of the monochromator entrance slit just above the top of the primary zone, *i.e.*, about 1 cm high in the separated flame. Stray radiation from the primary zone was screened from the slit by a small metal shield placed adjacent to the flame. The top of the flame was screened from the slit in a similar way so that the only radiation from the flame entering the slit was from a completely nitrogen-shielded region of the interconal zone *ca.* 2·5 cm high.

Effect of acetylene flow on bismuth emission at 306·8 *nm*

The emission from an aqueous solution sprayed into the nitrogen-separated air–acetylene flame was recorded at different acetylene flow-rates, with a constant nebulizing air-pressure of 28 psi. These results are plotted in Fig. 2*a*. The acetylene pressure is expressed as head (in cm) of di-n-butylphthalate in the fuel-pressure manometer of the spectrophotometer gas-control unit. The stoichiometric flame corresponded to a pressure of 9·2 cm. The bismuth emission increases almost linearly as the flame is made more fuel-lean and reaches a peak in the very fuel-lean flame. This flame was not used for actual determinations as it also produced a high background and signal noise level.

Effect of acetylene flow on flame background emission at 306·8 *nm*

This was investigated by measurement of the increase in flame emission at 306·8 nm when the acetylene pressure was reduced progressively below that necessary for a stable fuel-rich flame (10·0 cm). The values obtained are plotted in Fig. 2*b* from which it can be seen that at first there is a slow rise until, in the fuel-lean flame, the background emission begins to increase rapidly.

Effect of acetylene flow on the stability of the flame emission at 306·8 *nm*

In the ordinary air-acetylene flame, the OH band emission causes a high noise level in the measurement of atomic emission signals at 306·8 nm with any fuel setting of the flame, and it is this factor (as much as the actual magnitude of the flame background) which chiefly restricts the detection limit of bismuth to around 1000 ppm. In the separated flame, therefore, it is just as important to select the fuel mixture giving a low noise level as that giving the lowest background intensity. The variation of noise level with fuel flow at an air pressure of 28 psi is shown in Fig. 2*c*. For the purposes of this

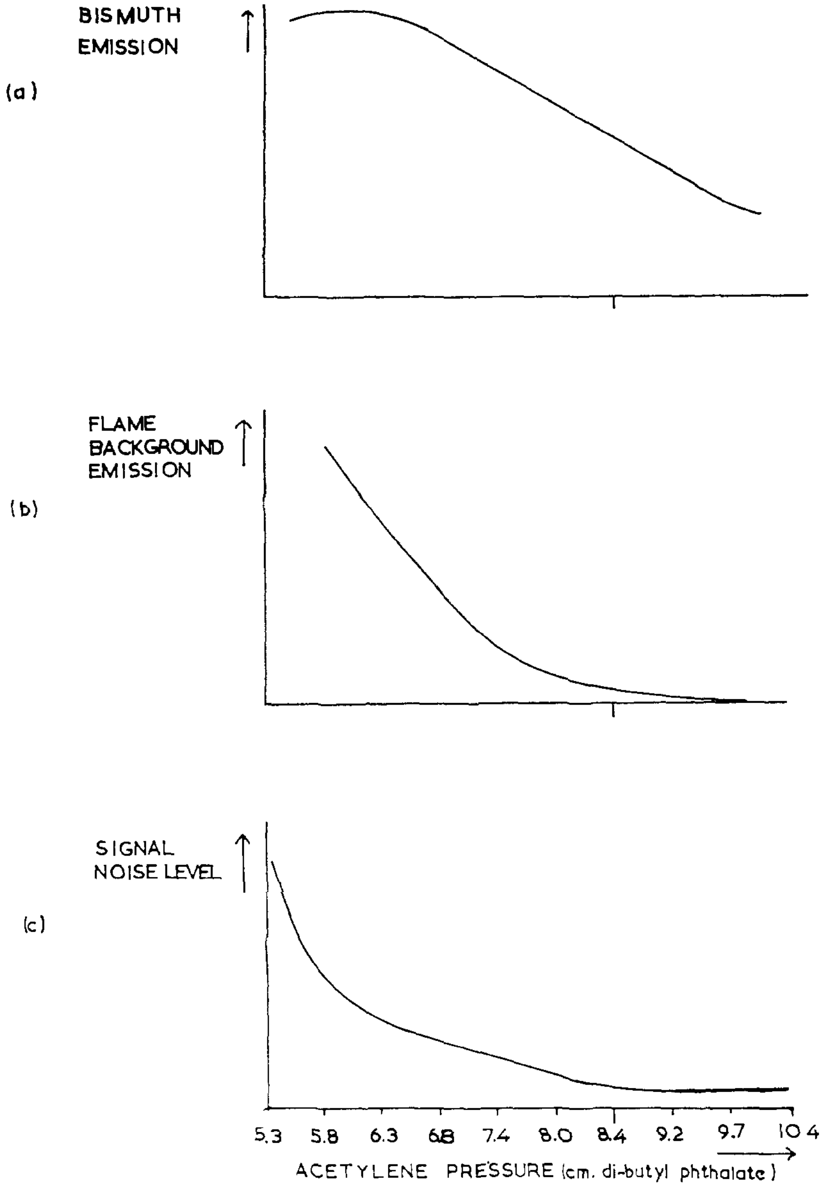

FIG. 2—(*a*) Effect of acetylene pressure on thermal emission of bismuth at 306·8 nm. (*b*) Effect of acetylene pressure on flame background emission at 306·8 nm. (*c*) Effect of acetylene pressure on signal noise level for bismuth emission at 306·8 nm.

particular graph, the noise level was taken as the distance between opposite extremities of a recorder trace produced during a period of 60 sec by the flame emission at 306·8 nm from an aqueous (100-ppm) bismuth solution. It can be seen that the noise level is almost constant down to a fuel pressure setting of 8·2 cm.

Selection of optical flame conditions

The following conclusions may be drawn from the graphs in Fig. 2.

(*i*) The bismuth emission can be increased linearly by using a more fuel-lean flame, long beyond the point where the extra flame background and noise make this a useful means of increasing the sensitivity. The decisive factors in choosing the best flame settings must, therefore, take into account the background intensity and noise levels.

(*ii*) The rate of increase of background emission and signal noise with decreasing fuel flow-rate is quite slow between acetylene manometer readings of 10·4 and 8·4 cm, but below this both start to increase quite rapidly. The separated flame obtained at an acetylene pressure of 8·4 cm was, therefore, chosen for the bismuth determinations. This acetylene pressure produces a slightly fuel-lean flame.

Determination of bismuth in aqueous solution

A stock solution containing 1000 ppm of bismuth was prepared by dissolving 1 g of pure bismuth metal in dilute nitric acid and diluting to 1 litre with distilled water. Standard solutions in concentrations down to 5 ppm were prepared by appropriate dilution of this solution, and a linear calibration curve at 306·8 nm could be prepared for bismuth concentrations of 5–200 ppm. The absolute detection limit for bismuth (defined as a signal:noise ratio of unity) was found to be 2 ppm.

Determination of bismuth in aqueous-ethanolic solution

Although the determination of bismuth at concentrations down to 5 ppm is adequate for many purposes, it was felt that the sensitivity could be usefully extended by the use of organic solvents to increase the efficiency of nebulization of the samples. The role of the solvent in this process has been concisely reviewed by Mitchell.[6] There are two main ways by which the desired effect can be achieved.

(*i*) The use of water immiscible solvents and a solvent extraction technique, such as that developed for bismuth by Willis.[7]

(*ii*) The use of water-miscible solvents which may be directly added to the aqueous analysis solution to enhance the emission intensity.

The former method was rejected because, although a greater enhancement of emission can be expected, much more sample preparation is entailed. Ethanol was chosen as the solvent for addition to the aqueous sample solutions, and the effect on the flame of spraying different mixtures is shown in Fig. 3. The emission from the separated flame with an acetylene pressure of 9·5 cm (*i.e.*, very slightly fuel-rich) was noted when water was sprayed and then the acetylene pressure was reset for each ethanolic solution sprayed so that exactly the same flame and emission were obtained. A point of inflexion occurs for solutions containing between 50 and 60% ethanol, and it was found that the maximum nebulizer uptake-time of ethanol-water mixtures also occurs at this point.

With the low bismuth concentrations required, solutions containing up to 60%

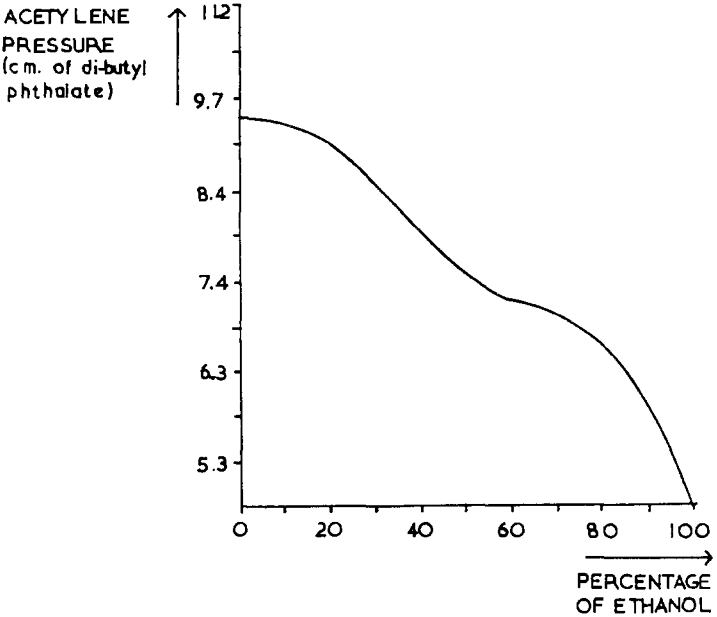

Fig. 3.—Effect of variation in composition of nebulized ethanol-water solutions on acetylene pressure required to maintain low background stable flame.

ethanol could be prepared without any special precautions. At higher alcohol concentrations, however, there was a tendency for precipitation to occur after the solutions had been standing for several hours. A plot of bismuth emission intensity *vs.* alcohol concentration was, therefore, prepared for solutions containing up to 60% ethanol (Fig. 4). Each reading was taken after adjustment of the zero control of the instrument during spraying of a blank solution containing the corresponding amount of ethanol. The separated air-acetylene flame was used at 15 psi of air instead of the 28 psi used for aqueous solutions, because it was found that at ethanol concentrations above 30%, the higher air pressure gave a much more unsteady flame with only a relatively small increase in bismuth emission to compensate for it. It can be seen from Fig. 4 that the emission increases sharply up to *ca.* 55% ethanol. As higher ethanol concentrations also give increased flame background, 50% aqueous ethanol was selected for bismuth determinations. This gives about a seven-fold increase in sensitivity over aqueous solutions. The optimum acetylene pressure was found, by the method previously described for the aqueous solutions, to be 4·8 cm. Allowing for the lower air pressure and the action of the ethanol as a fuel, this setting corresponded to the value used for aqueous solutions and the two flames were of very similar appearance.

A linear calibration curve could be prepared for solutions containing 1–10 ppm of bismuth and the absolute detection limit was found to be 0·3 ppm.

Atomic-Fluorescence Spectroscopy

The source, monochromator and detection system employed for the determination of zinc and cadmium by atomic fluorescence in the shielded flame were similar to those described by Dagnall, West and co-workers.[3,8]

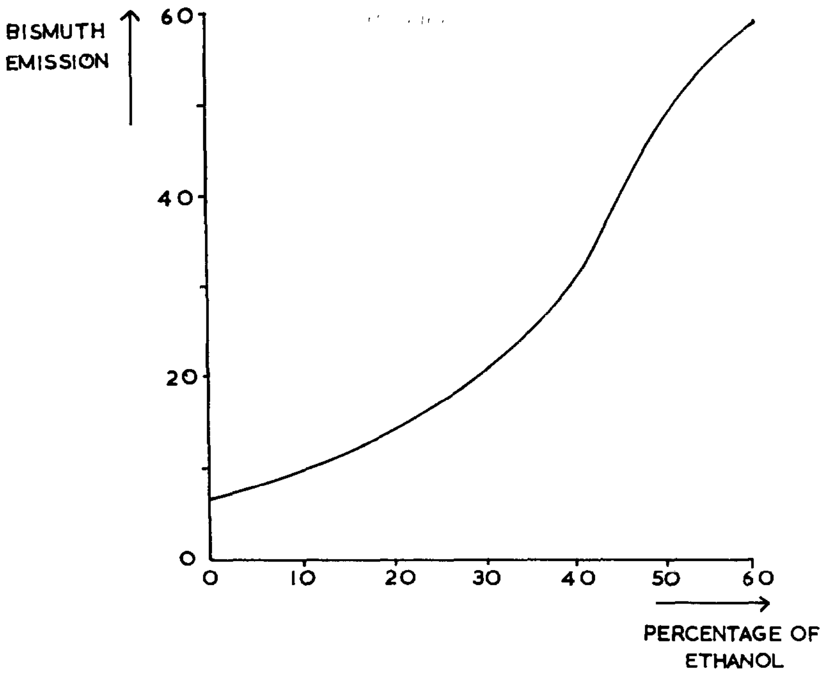

Fig. 4.—Effect of composition of ethanol-water solvent on bismuth emission intensity at 306·8 nm.

Operating conditions and results for zinc

The optimum experimental conditions established were: zinc discharge-lamp current 1·5 A; analysing monochromator slitwidth 2·0 mm; air-pressure to flame 15 psi, acetylene manometer setting 4·8 cm; nitrogen shielding-gas flow-rate 10 l./min; fluorescence measurements made at a height in the flame such that the centre of monochromator slit was 3 cm above burner head. The wavelength of measurement was 213·9 nm, which corresponds to the wavelength of the resonance line for the transition $^1S_0 - {}^1P_1$. No fluorescence emission was observed at other wavelengths for zinc. With these experimental conditions, linear calibration graphs were obtained at 213·9 nm over the ranges 0·01–0·1 and 0·001–0·01 ppm zinc with the separated flame. The limit of detection, corresponding to a signal:noise ratio of unity, was found to be 2×10^{-4} ppm in aqueous solution.

When the shielding gas was not used, and the optimum instrumental and fuel flow-rate conditions for fluorescence in the conventional air-acetylene flame were established, less sensitivity was obtained for zinc. Linear calibration groups at 213·9 nm were obtained over the range 0·01–0·1 ppm. The higher background and noise level resulted in a detection limit of 2×10^{-3} ppm zinc in aqueous solution.

Operating conditions and results for cadmium

The optimum experimental conditions of cadmium discharge-lamp current, monochromator slitwidth, fuel and air pressures and nitrogen flow-rate, were established to be the same as those employed for zinc. Fluorescence measurements were made at a height in the flame such that the centre of the monochromator slit was 3·0 cm above the burner head. The wavelength of measurement was that of the 228·8 nm resonance line, corresponding to the $^1S_0 - {}^1P_1$ transition. Fluorescence emission was also observed at the 326·1 nm resonance line, although this was much weaker than that at 228·8 nm.

With these experimental conditions, linear calibration graphs were obtained at 228·8 nm over the ranges 0·01–0·1 and 0·1–1·0 ppm cadmium with the shielded flame. The limit of detection for cadmium at 228·8 nm, defined as above, was found to be 5×10^{-4} ppm in aqueous solution. A detection limit of 1 ppm in aqueous solution was obtained when atomic fluorescence was measured at the 326·1 nm resonance line.

With the conventional air-acetylene flame, fluorescence emission for cadmium at 326·1 nm was not observed against the high background emission, and the detection limit obtained for the 228·8 nm emission was 2×10^{-3} ppm in aqueous solution.

Optimal conditions of burner height and fuel flow-rate differ only very slightly for atomic-fluorescence measurements in the separated and conventional flames. The lower flame background of the separated flame permits the use of higher instrumental sensitivities without saturation of the electronics. The low noise levels which result from the flame and detection systems under these conditions result in benefit to the detection limits obtained.

CONCLUSION

Separation of the secondary diffusion zone of the premixed air-acetylene flame by shielding from atmospheric oxygen with nitrogen gas, produces an interconal zone of very low radiative background. Atomic line signal-to-flame-background intensity ratios obtained in the flame photometry of elements introduced into the flame are, therefore, greatly increased. This is exemplified by the sensitive determination of bismuth by flame emission spectrophotometry at 306·8 nm where intense background from the strongest OH band system at 306·4 nm occurs in conventional flames but is virtually absent in the shielded flame.

The method of separation by nitrogen-shielding, described here, possesses several pronounced advantages over the mechanical method which we previously employed.[1] A wide range of fuel-air mixture strengths can be used, organic solvents may be nebulized, and no separator contamination problems are encountered.

The low background and noise levels of the nitrogen-separated flame can also be exploited to advantage in atomic-fluoresence spectroscopy. This is evident from a comparison of the detection limits obtained with the separated and conventional flames for the determination of cadmium and zinc by atomic-fluorescence spectroscopy. In a comparison of the suitability of the air–hydrogen, air–propane and air–acetylene flames for the determination of zinc by atomic-fluorescence spectroscopy, Dagnall, Thompson and West[3] concluded that the air–acetylene flame was the least suitable, chiefly because of the high background emission encountered. For the determination by atomic-fluorescence spectroscopy of less volatile elements, however, the higher temperature of the air–acetylene flame may be required to generate a sufficient population of ground-state atoms. Under these conditions the utility of the separated flame to lower the flame radiative background would undoubtedly be of even greater advantage.

Acknowledgement—We wish to thank Aluminium Laboratories Limited for the loan of a Unicam spectrophotometer, and for financial support to one of us (R. S. H.). We also thank the Science Research Council for the award of a research studentship to M.S.

Zusammenfassung—Die primäre und sekundäre Kombinationszone einer Luft-Acetylen-Flamme wurden durch einen parallel zur Flamme fließenden Stickstoffstrom getrennt der den Zutritt von atmosphärischem Sauerstoff zur Flammenbasis verhindern sollte. Die Flamme ist in einem großen Bereich des Mischungsverhältnisses Brennstoff-Luft stabil und organische Lösungsmittel konnen ohne Schwierigkeiten angesaugt werden. Wegen des geringen Flammenuntergrundes können thermische Emissionsmessungen und Atomfluoreszenzmessungen mit hoher Empfindlichkeit ausgeführt werden. Zum Beispiel wurde Wismut im Bereich 5–200 ppm durch seine thermische Emission bei 306,8 nm bestimmt, wobei die Nachweisgrenze in wäßriger Losung 2 ppm betrug, sowie im Bereich 1–10 ppm in 50% alkoholischer Lösung mit einer Nachweisgrenze von 0, 3 ppm. Zink und Cadmium wurden in dieser Flamme bei 213,9 und 228,8 nm durch Atomfluoreszenzspektroskopie mit Nachweisgrenzen von 2.10^{-4} ppm bzw. 5.10^{-4} ppm bestimmt, wobei DampfEntladungslampen als Anregungslichtquellen verwendet wurden. Die erhaltenen Ergebnisse stellen gegenüber dem, was in einer konventionellen Luft-Acetylen-Flamme mit denselben Methoden erreichbar ist, eine beträchtliche Verbesserung dar.

Résumé—Les zones de combinaison primaire et secondaire d'une flamme air-acétylène ont été séparées par un courant d'azote s'écoulant parallèlement à la flamme pour éviter l'accès de l'oxygène atmosphérique à sa base. La flamme est très stable dans un large domaine de concentrations du mélange combustible-air et des solvants organiques peuvent être aspirés sans difficulté. Le faible fond de flamme permet aux mesures d'émission thermique et de fluorescence atomique d'être faites avec une haute sensibilité. Le bismuth, par exemple, a été dosé dans le domaine 5–200 p.p.m. par son émission thermique à 306,8 nm, avec une limite de détection de 2 p.p.m. en solution aqueuse et dans le domaine 1–10 p.p.m. avec une limite de détection de 0,3 p.p.m. en solution éthanolique à 50%. Le zinc et le cadmium ont été déterminés à 213,9 nm et 228,8 nm par spectroscopie de fluorescence atomique dans cette flamme avec des limites de détection de 2×10^{-4} p.p.m. et 5×10^{-4} p.p.m. respectivement, des lampes à décharge à vapeur étant utilisées comme source d'excitation. Les résultats obtenus représentent une amélioration considérable par rapport à ceux accessibles par les mêmes méthodes dans une flamme air-acétylène ordinaire.

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EVALUATION OF THE LANTHANUM FLUORIDE MEMBRANE ELECTRODE RESPONSE IN ACIDIC SOLUTIONS

THE DETERMINATION OF THE pK_a OF HYDROFLUORIC ACID

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Summary—Measurements made with a combination of glass and lanthanum fluoride membrane electrodes in solutions which are strongly acid but varying in ionic strength have been used to calculate the dissociation constant of hydrogen fluoride and to validate the response of the latter electrode in strongly acidic media containing fluoride ions.

THE measurement of fluoride activity has been greatly facilitated since the introduction of the single-crystal fluoride membrane electrode.[1] The construction and performance of this electrode has been described as well as its use as an indicating electrode in potentiometric titrations.[2] In aqueous solutions, the response of this electrode is a function of the hydrogen ion concentration. At lower pH values, the fluoride activity is markedly affected owing to the formation of hydrogen fluoride, while at higher pH values the hydroxide ion, which is iso-electronic with fluoride, interferes. No thorough investigation describing the response of the fluoride electrode in acidic media has been reported. If the electrode is not affected directly by the hydrogen ion, the use of this electrode should afford an interesting and novel way of determining the ionization constant of the weak acid, HF.

It is generally concluded that a dilute aqueous solution of fluoride contains the species F^-, HF, and HF_2^-. Determination of the ionization constant of HF in aqueous solution has been made by several methods.[3–5] Broene and DeVries,[4] with their potentiometric study of the hydrogen electrode in aqueous fluoride solutions, have shown that at 25°, K_a for HF is $6{\cdot}71 \times 10^{-4}$ mole.l.$^{-1}$. The formation constant for the homoconjugate ion, HF_2^-,

$$HF + F^- = HF_2^- \qquad K_f = [HF_2^-]/[HF][F^-]$$

has been reported by several workers[2,4] to be approximately 4·0 l.mole^{-1}. Measurements of the equilibrium constant as a function of ionic strength have not been reported.

Theory of measurements

Potential measurements were made in a series of solutions, each series composed of constant ionic strength mixtures of sodium perchlorate and perchloric acid. Sodium

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fluoride was added to each solution to a formal concentration of 0·001M. Measurements were taken of both the potential of the glass electrode (a measure of hydrogen ion activity) and the fluoride membrane electrode (fluoride ion activity) in each test solution.

The total fluoride concentration will be distributed amongst various species in the solution (in a manner specified by the pH)[3] so that:

$$[F_T] = [F^-] + [HF] + 2[HF_2^-]$$

Substitution of K_f, the formation constant for HF_2^-, and K_a, the acid dissociation constant, gives:

$$[F_T] = [F^-] + [H^+][F^-]/K_a + 2K_f[H^+][F^-]^2/K_a.$$

Subtracting $[F^-]$ and factorizing yields:

$$[F_T] - [F^-] = \frac{[F^-][H^+]}{K_a}\{1 + 2K_f[F^-]\}.$$

Since K_f has been shown to be approximately 4·0 and, at a maximum, the value of $[F^-]$ is $10^{-3}M$,

$$1 \gg 2K_f[F^-] < 8 \times 10^{-3}, \quad \text{or}$$

$$\frac{[F_T] - [F^-]}{[F^-]} = [H^+]/K_a.$$

Taking common logarithms results in:

$$\log([F_T] - [F^-]) - \log[F^-] = \log[H^+] - \log K_a.$$

In this investigation, the fluoride concentration, as determined by the membrane electrode, was maintained at such a level (by the addition of perchloric acid) that $[F^-]$ was, in the worst case, only 10% of $[F_T]$. Thus we can write with confidence

$$\log[F_T] - \log[F^-] = \log[H^+] - \log K_a.$$

Although, up to now, no activity corrections have been made, a similar expression could be written:

$$\log[F_T](f_{F^-}) - \log[F^-](f_{F^-}) = \log a_{H^+} - \log K_a{}^\circ \qquad (1)$$

where (f_{F^-}) is the molar activity coefficient and a the activity. Changing signs and writing $\text{pH} = -\log a_{H^+}$ yields:

$$\log[F^-] - \log[F_T] = \text{pH} + \log K_a$$

The fluoride membrane electrode yields the usual Nernstian behaviour,[2]

$$E_{F^-} = E^\circ - \frac{RT}{F}\ln[F^-](f_{F^-}).$$

On variation of the fluoride concentration in a constant ionic strength system (a solution containing a large excess of sodium perchlorate), the response of this electrode can be readily determined as a function of ionic strength. Thus the fluoride *concentration* can be determined at any particular ionic strength by measurement of fluoride electrode potential. The response of the electrode will be given by

$$E_F = E' - S\log[F^-]$$

where S is the empirically determined slope which defines the electrode response at each particular ionic strength and E' is a similar formal potential. Substitution into equation (1) and rearrangement yields:

$$\Delta E_F/S = \frac{E_{F_T} - E_F}{S} = \text{pH} + \log K_a.$$

Here E_{F_T} is the fluoride potential measured in the absence of added hydrogen ion and E_F is the potential measured as a function of pH. Plotting the change in fluoride electrode potential divided by S, against the pH, should yield a linear relationship of slope 1·00 with intercept log K_a.

EXPERIMENTAL

Solutions were prepared from reagent grade chemicals and were stored in polyethylene containers. Shortly before use, the individual test solutions were prepared by diluting requisite amounts of various stock solutions to volume in 100-ml volumetric pyrex flasks. (There is good evidence that fluoride in millimolar concentrations will not attack pyrex glassware as long as the solution is kept below 60°).[6] The test solutions were transferred to polyethylene beakers, placed in the constant-temperature bath, the electrodes inserted, and solutions stirred with a teflon stirring rod. Replicate determinations agreed within ±1·0 mV.

Three electrodes were used in this investigation. Fluoride-ion measurements were made with an electrode supplied by Orion Research, Inc., and hydrogen-ion measurements were obtained with a Sargent Wide-Range glass electrode. These potentials were measured *vs.* a calomel reference electrode. This electrode was filled with saturated sodium chloride solution to prevent the precipitation of potassium perchlorate which occurs at the liquid-junction solution interface with the conventional calomel electrode. Potential measurements were made with a Beckman Model 76 Expanded pH Meter modified to allow the application of a variable d.c. signal in series with the reference electrode. The magnitude of this bucking e.m.f. was measured with a potentiometer. In this way, the expanded scale (200 mV full scale) could be used throughout the measurements. Potential measurements were reproducible to better than 1 mV. All measurements were performed at 25·0 ± 0·2°.

RESULTS

Determination of fluoride electrode response coefficients

Measurements were made by introducing various amounts of 0·100M sodium fluoride (with a Manostat Digi-Pet) into 75·0 ml of a sodium perchlorate solution at the desired ionic strength. The measurements were carried out to span more than one decade of fluoride concentration, the total fluoride concentration varying from approximately 10^{-5} to $10^{-3}M$. At least 15 determinations were made at each ionic strength. Plots of E_{F^-} *vs.* log [F$^-$] yielded linear curves of slope varying from very close to the theoretical value (at 25°) of 59·2 mV/decade of fluoride ion concentration to a value of 57·1 mV/decade in a solution of 1·0M sodium perchlorate. These slopes were obtained by a least squares analysis of the potentials. (Individual values yielded a linear relationship when plotted *vs.* the square root of ionic strength.) These values of S were used in subsequent data analysis.

Evaluation of K_a

Constant ionic strengths of 0·050, 0·100, 0·200 and 0·500M were obtained by mixing the requisite amounts of perchloric acid and sodium perchlorate. The potential of the fluoride electrode measured in a solution at the specified ionic strength containing only sodium perchlorate was used as E_{F_T} and potentials found in the various acid-containing solutions were subtracted from it to obtain ΔE, at least 10 experimental points being obtained at each ionic strength. These results were then plotted as $\Delta E/S$ *vs.* the measured hydrogen-ion activity. The activity of the hydrogen ion was determined by measuring the glass electrode potentials and comparing them with values determined for activity standards at pH = 2·00 and pH = 4·00 and assuming a change of 59·1 mV/decade of hydrogen-ion activity. The results, along with the slope values described above, are shown in Table I.

TABLE I

Ionic strength		S*	Goodness		
μ, *M*	$\sqrt{\mu}$	*mV/log* [F^-]	of fit†	Slope‡	Intercept¶
0·050	0·224	59·05	0·9977	0·996	−3.044
0·100	0·316	59·00	0·9953	0·990	−3.031
0·200	0·447	58·90	0·9983	1·007	−2·938
0·500	0·707	58·80	0·9990	1·011	−2·751

* Experimental slope for fluoride ion electrode response.
† Least-squares analysis, fit to linear equation.
‡ Slope of experimental curve, least-squares adjusted.
¶ Intercept of experimental curve, least-squares adjusted.
[The error in these measurements is approximately 0·5%. Potential measurements in each series spanned approximately 150 mV.]

Finally, the values of the graphically determined equilibrium constants were plotted *vs.* the square root of ionic strength, yielding a value of log K_a = −3·189 at zero ionic strength, corresponding to an acid ionization constant of 6·46 × 10^{-4} mole.l.$^{-1}$.

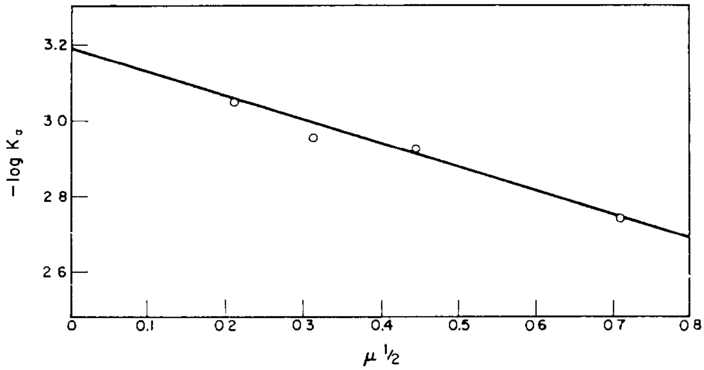

FIG. 1.—Variation of equilibrium constant with ionic strength.

CONCLUSION

The agreement of the ionization constant with that found by other workers indicates that the method is essentially sound and, moreover, that the fluoride-ion membrane electrode continues to function as an indicator of fluoride-ion activity in acidic solutions.

The determination of the equilibrium constant in the way described above raises some interesting points. No assumptions need be made concerning the equality of anionic and cationic activity coefficients of the same charge type. Moreover, no assumption need be made concerning activity coefficients of the fluoride ion, since the derivation cancels out this term. Measurements obtained in this way, that is, at constant ionic strength, offer the greatest possibility of minimizing liquid-junction potential errors. In such a cell as that used here, the junction potential during the measurements made to evaluate the electrode response in constant ionic strength media should remain approximately constant. The constancy in the second series of experiments, the determination of K_a, is of interest. The two parameters plotted, ΔE and pH, are both derived from potentials measured *vs.* the same reference electrode. Changes of liquid-junction potential would affect each potential measurement in the same way, thus in no way affecting either of the two desired parameters, the slope and intercept. Thus, the uncertainty in this measurement caused by changes in liquid-junction potential is considerably smaller than that found in most potentiometric equilibrium-constant determinations. This, perhaps, is evident in the experimental results and in the fact that the least-squares slopes do not deviate significantly from unity.

Zusammenfassung—In stark sauren Lösungen verschiedener Ionenstärken mit einer Kombination aus Glas- und Lanthanfluoridmembranelektroden durchgeführte Messungen wurden zur Berechnung der Dissoziationskonstante von Fluorwasserstoff verwendet sowie zur Prüfung des Ansprechens der zuletzt genannten Elektrode in fluoridhaltigen stark sauren Lösungen.

Résumé—On a utilisé des mesures effectuées avec une combinaison d'électrode de verre et d'électrode à membrane de fluorure de lanthane dans des solutions qui sont fortement acides mais de force ionique variable pour calculer la constante de dissociation de l'acide fluorhydrique et rendre valable la réponse de la dernière électrode en milieux fortement acides contenant des ions fluorure.

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DETERMINATION OF SUBMICROMOLAR CONCENTRATIONS OF FLUORIDE IN BIOLOGICAL SAMPLES*

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Summary—The fluorescence of a Morin–thorium complex provides a more sensitive fluoride reagent than has been previously used. It has immediate stability and a linear response to fluoride up to 50% reduction in fluorescence. The values for serum fluoride, as measured with this reagent after diffusion at room temperature, agree with those obtained with the fluoride electrode and with those predicted by the renal clearance of radioactive fluoride. The relative standard deviation when measuring $10^{-6}M$ fluoride in 2 ml of serum is ±10%.

THERE is a marked disagreement about the concentration of fluoride in the serum of persons drinking fluoridated water. Singer and Armstrong[1] claimed in 1967 that it is at least five times the value reported by Smith, Gardner and Hodge[2] in 1950 and by Taves[3] in 1966. Recently it has been appreciated that clearance of radioactive fluoride, $^{18}F^-$, together with a known concentration of stable fluoride in the urine, provides an independent determination of the concentration of fluoride in the serum.[4] Renal clearance is expressed as the number of ml of plasma that would have to be completely cleared of a substance by the kidneys to yield the amount of that substance collected in the urine in 1 min.[5] This can be expressed mathematically as follows.

$$\text{Renal clearance} = \frac{\text{urine concentration} \times \text{urine flow (ml/min)}}{\text{serum concentration}} \qquad (1)$$

If renal clearance of $^{18}F^-$ is the same as that of $^{19}F^-$, then, substituting and solving for the serum concentration of $^{19}F^-$:

$$\text{Serum } ^{19}F^- \text{ concentration} = \frac{^{19}F^- \text{ urine concentration} \times \text{urine flow (ml/min)}}{\text{renal } ^{18}F^- \text{ clearance}} \qquad (2)$$

The normal clearance of $^{18}F^-$ averages 50 ml/min,[4] the normal urine flow-rate is 1 ml/min and the average urine fluoride concentration is $50\mu M$ (1 ppm) in specimens collected from persons drinking fluoridated water.[6] Substituting these values in equation 2 gives an average serum fluoride concentration of $1\mu M$ (0·02 ppm). This concentration is too low for published methods to measure accurately, explaining, perhaps, why the literature shows a confusingly wide range of values for normal serum fluoride concentrations.

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Smith, Gardner and Hodge report values that average 1·7μM (0·03 ppm), near the calculated 1·0μM.[2] Their method, however, requires 50 ml of blood, so duplication is not easy and the blank is seven times the amount of fluoride being measured.[7] This, and the involved procedure, makes it appear likely that the wide range of values they found (0–4μM) is due to analytical difficulty rather than to basic human variation. Singer and Armstrong give values that average 7·5μM (0·15 ppm),[8] suggesting that they are measuring something in addition to fluoride in serum. Smith and Hodge, in their detailed review,[9] and Smith more recently,[10] list numerous reports of values that are generally much higher than those of Singer and Armstrong. Hall, using a new reagent that appears to be more sensitive than previous colorimetric reagents, says the concentration is usually less than 5μM in blood.[11]

Improvement in the accuracy of trace fluoride determination requires a more sensitive reagent and a reduction in the blank value. The use of plastic microdiffusion dishes limits the quantity of serum that can be used to about 3 ml. This represents 3 nmoles (0·06 μg) of fluoride or only 3 % of the maximum of Singer and Armstrong's working curve, since the range they used is 0–100 nmole (2·0 μg).

More sensitive reagents have been proposed, based on quenching of the fluorescence of various dye-aluminium complexes by fluoride.[12,13] The most sensitive and quickly stabilized fluorescent reagent, reported by Willard and Horton in 1952, is a Morin (pentahydroxyflavone) aluminium complex.[12] Bouman, however, found it to be insufficiently stable and the response to fluoride poor at low concentrations; his modifications include using ice-cold reagents and rapid reading of the fluorescence.[14] These changes and the lack of biological studies applying these methods suggest that a better fluorescent reagent is needed.

Morin with thorium has been used as a fluorescent indicator of the titration end-point for large quantities of fluoride[15] so it appeared worth testing as a reagent. In the present study, Morin and thorium were found to be adequately sensitive, to give a standard curve with a long linear portion, and to have immediately stable fluorescence. Preliminary results with this new reagent for analysis of serum fluoride samples after diffusion at room temperature, indicated that the average normal serum fluoride concentration was 0·7μM,[3] *i.e.*, very close to the calculated value.

The reproducibility, however, was not satisfactory for these low levels, probably because the diffusion blank was 2–3 times the amount of fluoride in the samples. While looking for the source of the blank it was found that the silicone grease used to seal the dishes was in fact involved in the diffusion of fluoride. The simplest silicone, hexamethyldisiloxane, greatly accelerated the transfer of fluoride.[16] This allowed the use of larger samples so that accurate measurements could be made with the fluoride electrode, enabling comparison to be made with the values obtained by the present method.

EXPERIMENTAL

Apparatus

The diffusion dishes, scintillation counter and rotary shaker were the same as described previously.[16]

The test-tubes were disposable polystyrene plastic, 17 × 100 mm (large) and 12 × 75 (small) made by Falcon Plastics, 5500 West 83rd Street, Los Angeles, California 90045. These tubes are used for receiving the trapping solution, neutralizing, and reading in the fluorimeter. Aluminium centrifuge cup adapters were made to accommodate the disposable plastic tubes snugly in order to prevent breakage when spinning down the clot or the protein precipitate from serum.

The fluorimeter was an Aminco Fluoro-microphotometer in which the tube receptacle had been enlarged to accept the 17-mm diameter tubes. The filters were 2A-12 and 47B for the 420 and 510 mμ excitation and emission wavelengths. (The optimum wavelengths were determined on an Aminco-Keirs Spectrophosphorimeter.) A voltage stabilizer (Sola, 0·485 A) was used to decrease the fluctuations of the fluorimeter. A light shield is mounted over the tube receptacle to make it possible to rotate the tubes by hand while reading the fluorescence. This is an advantage because it allows increased speed in reading and because any serious imperfections in the tubes can be easily detected from fluctuations of the needle position. A convenient light shield was made from a cardboard box, 5 × 5 × 12 in., mounted horizontally in a position that allowed easy introduction of the tubes through the length of the box into the tube receptacle while the operator was seated in front of the fluorimeter. The box was covered inside and out with black cloth to minimize stray light.

An Orion fluoride electrode(17) was used with a Beckman model G pH meter.

A Vortex mixer (Scientific Industries Inc.) was used in the titration step.

Reagents

Distilled water is passed through a commercial demineralizing column and then redistilled from an all-glass still.

Hydrochloric acid, $6M$ saturated with the silicone HMDS (hexamethyldisiloxane, Dow Corning 200 fluid, 0·65 centistokes, Dow Corning, Midland, Michigan) is prepared by shaking 200 ml of the acid with 25 ml of the silicone for 2 min in a separatory-funnel. The silicone layer is discarded since it will contain fluoride extracted from the acid, and a fresh 25 ml of HMDS is added so that the acid will remain saturated and aliquots can be drawn off as needed. To remove the silicone from the acid used for neutralization of the trapping solution, the acid prepared as above is boiled until its volume is reduced by one-half. The acid is then diluted to $1M$ and $0{\cdot}05M$ for use in titration.

The stock fluorescence reagent consists of $0{\cdot}001M$ Morin (2′,3,4′,5,7-pentahydroxyflavone) and $0{\cdot}0005M$ thorium nitrate in 95% ethanol. The stock reagent is stable for several months. The diluting solution consists of 100 ml of 95% ethyl alcohol and 2 ml of $11{\cdot}4M$ perchloric acid diluted to 1 l. with water. The working reagent is 2 ml of stock reagent made up to 100 ml with diluting solution.

Cleaning solution for glassware is made with 5 ml of stock reagent, 200 ml of alcohol and 10 ml of concentrated perchloric acid diluted to 2 l. with water. Glassware that did not drain properly was cleaned with RBS 25 (Fisher Scientific Co.), rinsed with distilled water, soaked in cleaning solution and rinsed again with water three or four times. Except for flasks and odd sizes of pipettes, only plastic ware is used. Much of it is disposable polystyrene and needs no cleaning. The polypropylene plastic ware sometimes used with serum should be cleaned (*e.g.*, with RBS) and rinsed with water.

The pH indicator solution consists of 0·1% phenolphthalein and 0·1% *p*-nitrophenol in 95% ethanol.

Radioactive carrier-free fluoride ($^{18}F^-$) was obtained from Western Nuclear Research, Power Drive, Buffalo, New York.

Low fluoride serum was obtained from a bitch and one of her pups which were fed a vitamin and mineral-supplemented milk diet.[18] Radioactive fluoride was administered in an infusion drip of $0{\cdot}0385M$ saline and 5% w/v glucose solution in order to produce a diuresis and nearly constant concentrations of $^{18}F^-$ during the time the urine and serum samples were obtained for calculation of the expected serum concentration. Equation (2) can be simplified after substitution for the renal clearance of $^{18}F^-$, from equation (1). The urine flows cancel since analyses of $^{18}F^-$ and $^{19}F^-$ were done on the same specimens.

$$\text{Serum } ^{19}F^- = \text{urine } ^{19}F^- \times \frac{\text{serum } ^{18}F^-}{\text{urine } ^{18}F^-}\,. \tag{3}$$

Procedure

A 1-mm hole is drilled in the lid of the diffusion dish about 7 mm from the edge and the lid is ringed with Vaseline where it will make contact with the dish. The acidified sample is placed in the outer chamber and 1 ml of $0{\cdot}1N$ sodium carbonate is placed in the centre compartment. After the lids are in position on all the samples, 0·5 ml of silicone-saturated hydrochloric acid is introduced into the outer chamber through the hole in the lid and the hole is quickly sealed with Vaseline.

The proteins are removed from serum by adding an equal volume of $6{\cdot}8M$ perchloric acid and centrifuging; only the supernatant liquid is used.

For normal urine, 1 ml is placed in the outer ring of a diffusion dish with 1 ml of $6{\cdot}8M$ perchloric acid. If the concentration of fluoride in the sample is thought to be above 100 μM (approximately 2 ppm) the urine is diluted.

Small acidified samples (2–4 ml) are diffused for at least 2 hr if agitated on the rotary shaker or

3 hr statically at room temperature. Large acidified samples (20 ml) are diffused for least at 6 hr with agitation on the shaker. (In this study large samples were run overnight for convenience.)

The trapping solution is transferred to the appropriate-size weighed plastic tube and titrated to near the colourless end-point of the pH indicator with 1*M* hydrochloric acid and finished with the 0·05*M* acid. Removal of carbon dioxide is accelerated during titration by vibrating with the vortex mixer, heating to 60° for 10 min and vibrating again. The final titration ends when 0·02 ml of 0·05*M* acid causes a change from a faint but definite yellow colour to no colour. The titration is not necessary when large amounts of fluoride are present, as in urine and bone. Water is then added to bring the samples and standards to a uniform weight, either 2 or 3 g (±5 mg). One ml of working reagent is added for each 7 nmole of fluoride expected. The solutions are mixed by inversion and read in the fluorimeter. The readings can be made at any time within 24 hr.

Fluoride electrode measurements are made on the neutralized diffusates from 10 ml of serum and compared with diffused standards which bracket the sample values. This determination can be followed by a measurement with the Morin–thorium reagent if the electrode is rinsed and the volume readjusted.

RESULTS

Figure 1 shows the standard curve with 1 ml of reagent. Deviation from a straight line is not apparent until the fluorescence is reduced by more than 50%. Also shown for comparison are the standard curves for the colorimetric reagents used by Singer and Armstrong[19] and by Hall.[11] When there is too much fluoride in the sample, *i.e.*, when the fluorescence cannot be read on the linear portion of the standard curve, more reagent may be added. This can be done even though it results in a change in acidity of the solution, because the optimum concentration of acid also shifts, as is seen in Fig. 2, so that the solution retains its maximum stability to small variations in acidity.

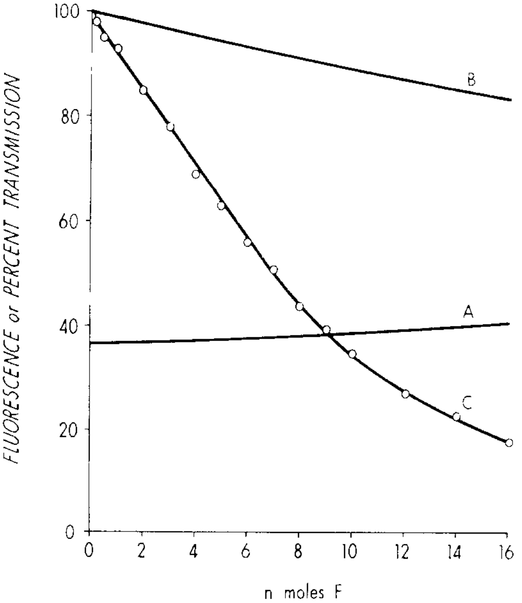

FIG. 1—*A*. Standard curve with zirconium–Eriochrome Cyanine R reagent as used by Singer and Armstrong.[19] *B*. Standard curve with lanthanum–Alizarin complexan reagent, taken from Hall.[11] *C*. Standard curve with 1 ml of Morin–thorium reagent.

The effects of sodium sulphate, phosphate, nitrate, and fluoride on the reagent are shown in Fig. 3. The reagent is seen to be more sensitive to the fluoride than to the sulphate and phosphate ions by factors of 20 and 40 respectively. The nitrate has no

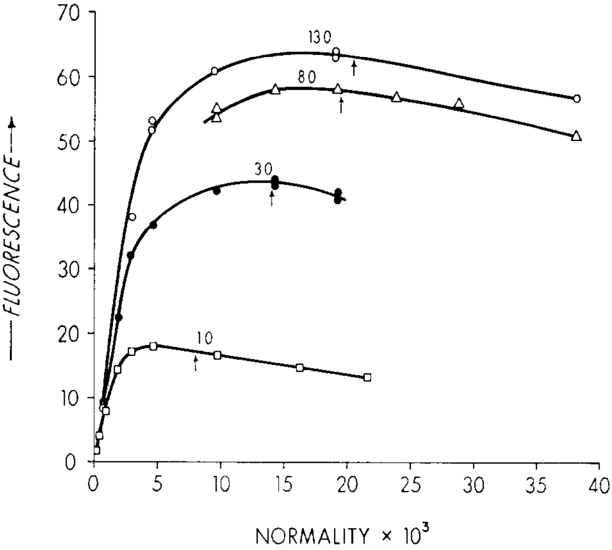

FIG. 2—Effect of varying the acid concentration of the Morin–thorium reagent, expressed as the final acidity after addition of 2 ml of 0 05*M* NaCl.

The figures by each curve indicate the number of ml of reagent taken and the arrows indicate the acidity when the reagent is made with the acid concentration given in the procedure.

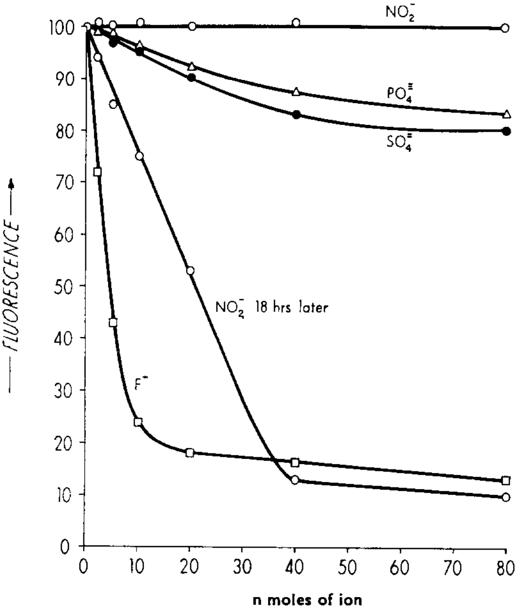

FIG. 3—Effect of various ions on fluorescence of reagent.

immediate effect but has a marked effect within 18 hr. Readings taken on the following day gave agreement with the originals within 5 fluorescence units for the sulphate and phosphate ions and 3 for the fluoride.

Large amounts of chloride have an effect on the concentration of acid necessary for maximum fluorescence, making an absolute comparison difficult. When the same amount of acid is used, the effect of chloride, perchlorate and nitrate is only 1/80000 that of fluoride.

To determine whether the HMDS in the trapping solution interferes with the reagent, two types of experiments were made. First, diffused blanks and standards were compared with non-diffused blanks and standards to see whether the slope of the standard curve is changed by HMDS. In three experiments with a total of fourteen 2-nmole and fifteen 6-nmole standards, the recovery of fluoride was 104 ± 11% (std. devn.) and 99 ± 5% respectively, after subtraction of the average blank for the experiment. This indicates that the HMDS in the trapping solution has no effect on the slope of the standard curve. The average blank for the three experiments ranges from 0 to 0·52 nmole, the standard deviation from 0·08 to 0·25 nmole. Second, comparison was of diffused blanks when different amounts of silicone had been added as HMDS-saturated hydrochloric acid to the outer ring. Comparison of diffusion blanks in sets of five without silicone or with up to twice the usual amount of it showed no trend and no statistical difference when read immediately and again after 1 hr. The maximum difference in the averages was 0·3 nmole, and the maximum standard error of the average was 0·18 nmole. Thus, within these limits there is no effect of HMDS. Reading the samples again the following day showed no consistent changes.

Since the protein of the serum is precipitated and only the supernatant is used for the analysis, it is important to know how much fluoride is left in the precipitate. The amount of fluoride in the protein precipitate can be estimated in three ways: (1) by the amount of $^{18}F^-$ not recovered in the trapping solution; (2) by direct counting of $^{18}F^-$ in the residual protein; (3) by an estimate of the fraction of solution left in the residual protein (% solution left in residual = [residual wt − protein wt/(acid + serum) wt − protein wt] × 100, protein weight taken as 70 mg/ml of serum). In an experiment with five samples the values obtained by these methods were 12·9% ± 2·0, 9·9% ± 0·5 and 10·5% ± 0·4 respectively. The last value is probably most nearly correct. The first is subject to losses in diffusion and the second to losses from $^{18}F^-$ left on the upper sides of the tube.

The effect on the serum fluoride concentration of prolonging the diffusion time from 2 to 18 hr was examined at two temperatures. No significant effect was noted at 26° but a statistically significant 20% increase occurred when the room temperature was 29–33° during prolonged diffusion.

Table I shows that the recovery of stable fluoride added to serum was about 97%.

Table II shows that the values obtained by the present method compare well with those of other methods. Singer and Armstrong's method[20] and the present method compare favourably for urine analysis. The fluoride electrode and the present method yield the same value in the analysis of serum. Equation (3) was used to calculate serum fluoride values for two dogs on a low fluoride diet. These values agree closely with those determined by the present method.

TABLE I.—RECOVERY OF STABLE FLUORIDE ADDED TO SERUM

Subject	Volume, *ml*	No. of samples	Original concentration, *μM*	Added, *μM*	Found, *μM*	Recovery, %
A	2	5	1·09 ± 0·06	2·5	3·41 ± 0·29‡	93
B	2	5	0·44* ± 0·10	2·5	2·84 ± 0·33‡	96
B	2	6	0·67* ± 0·10	0·5	1·15 ± 0·08‡	96
B	10	6	0·58 ± 0·07	0·5	1·07 ± 0·08‡	98
B	10	5	0·58 ± 0·07†	10·0	10·34 ± 0·17‡	98
C	2	5	0·10 ± 0·13	0·5	0·69 ± 0·17‡	118

* One value discarded, 2·0 and 1·2*μM* respectively.
† Not a repeat analysis.
‡ Standard deviation.
A = human
B = human citrated plasma
C = dog serum (low fluoride diet), 0·12*μM* ± 0·06 found in seven, 10-ml samples.

TABLE II.—COMPARISON WITH OTHER METHODS

Sample	Method	No. of samples	Result, *μM*	Results from present method, *μM*
Urine (1 ml)	Singer & Armstrong[20]	9	47·5 ± 7	50·2 ± 1·7† (5)‡
Serum D* (10 ml)	Electrode	4	0·88 ± 0·08	0·88 ± 0·02 (5)
Serum D (2 ml)				0·90 ± 0·04 (5)
Serum E (2 ml)	^{18}F ratio	4	0·44 ± 0·02	0·41 ± 0·09 (4)
Serum F (10 ml)	^{18}F ratio	3	0·06 – 0·09	0·09 – 0·14 (3)

* ^{18}F added to serum before separation of protein and used to correct for losses.
† Standard deviation.
‡ No. of samples.
D. Human.
E. Bitch.
F. Pup.

DISCUSSION

The validity of the serum fluoride concentrations as determined by the present method is supported by two independent techniques (Table II), in addition to evidence of the ability to recover about 97% of added stable fluoride (Table I), and as shown previously,[16] 98% of added radioactive fluoride from serum. The first involves comparison with the fluoride electrode after concentration and isolation of the fluoride by diffusion. Concentration is necessary because the normal serum fluoride level is in the range where the electrode starts to fail.[17] Isolation is important because bracketing standards and blanks are then in the same kind of solution. In the same experiment the completeness of fluoride recovery could be determined because the serum was labelled with $^{18}F^-$ before precipitation of the proteins.

The other involves experiments *in vivo*. Infusion of a solution of $^{18}F^-$ in dogs makes it possible to have a nearly constant concentration of $^{18}F^-$ in serum and in the urine so that the ratio can be determined accurately. Since there is no disagreement in the literature, or as shown here in Table III, on the determination of urinary fluoride, a value can be calculated for stable serum fluoride (equation 3). This value is shown to agree with the values measured by the new method.

The discrepancy in the values obtained by Singer and Armstrong[1] as compared to those of Smith, Gardner and Hodge[2] and of this method still exists. The difficulty may lie in the assumption that all of the fluoride in serum is exchangeable. The present method clearly measures the fluoride that is exchangeable with radioactive fluoride. No evidence is given, however, that this is all of the fluoride that is present in serum. It is possible that both values are correct. The evidence given here only indicates that fluoride which behaves like radioactive fluoride is being measured. There could be a non-exchangeable fluoride fraction present that is made available only after ashing, a technique employed by Singer and Armstrong in their distillation method.[19] Their diffusion method[20] probably does not measure the same thing in serum as their distillation method. Any organic acid which could diffuse at 60° is likely to bind with the zirconium in their reagent and look like fluoride. This could account for the continuing increase in the apparent fluoride concentration with prolonged diffusion[1] and the finding that most of the "fluoride" obtained under their conditions for diffusion is not heat-stable.[3] Since the apparent fluoride increases with the length of diffusion time the possibility exists that the agreement between their two methods is the result of selection of a time period which results in the same answer. The excess of apparent fluoride found in this work in an 18-hr diffusion at 29–33° is probably a reflection of the same problem.

The fluorescent reagent represents a considerable advance in sensitivity over the colorimetric reagents (Fig. 1). In addition, the fluorimetric system can tolerate much greater imperfections in the container without introducing serious error in the readings. This makes it possible to use disposable plastic tubes, thus eliminating the necessity to transfer samples, reducing reading time and making it possible to add additional reagent if high fluoride levels are encountered.

Only tentative comparisons can be made between the fluoride electrode and the Morin–thorium reagent. The present reagent has a clear advantage over the electrode in measuring samples in which the concentrations of fluoride vary markedly since the electrode has a memory problem when going from high concentrations to very low ones. Little can be concluded in this study about the relative sensitivity and reproducibility of the two methods since there are better meters which would be expected to improve the precision of the electrode and better optical systems for reading fluorescence. However, the sensitivity of the Morin–thorium reagent can be more than doubled even with the optical system used here. As yet it has not been possible to reduce the standard deviation for diffused samples when the additional sensitivity is used. The relative standard deviation in the present system is about 10% with 2-ml serum samples which are at least $1 \mu M$ in fluoride. For samples with less fluoride the standard deviation is less than $0{\cdot}2 \mu M$. If 10 ml of serum are available it is possible to reduce these limits by about half.

Smith, Gardner and Hodge[2] obtained results in which the mean value was similar to those presented here. The present method, in comparison with that of Smith, Gardner and Hodge,[7] achieves a 10-fold reduction in the amount of blood needed for an analysis and a 700-fold reduction in the blank.

Acknowledgement—I wish to thank Mrs. Joy Howe for her technical assistance.

Zusammenfassung—Die Fluoreszenz eines Morin–Thorium-Komplexes liefert ein empfindlicheres Reagens auf Fluorid als es bisher verwendet wurde. Es zeigt sofort stabil an und entspricht bis zu einer Fluoreszenzlöschung von 50% linear dem Fluoridgehalt. Die Fluoridwerte im Serum, wie man sie nach Diffusion bei Raumtemperatur mit diesem

Reagens mißt, stimmen mit denen überein, die mit der Fluoridelektrode gemessen und nach der Ausscheidung von radioaktivem Fluorid durch die Nieren vorausgesagt werden. Beim Nachweis von $10^{-6}M$ Fluorid in 2 ml Serum ist die relative Standardabweichung ±10%.

Résumé—La fluorescence d'un complexe Morin–thorium fournit un réactif du fluorure plus sensible qu'il n'a été antérieurement utilisé. Il a une stabilité immédiate et une réponse linéaire au fluorure jusqu'à une réduction de 50% de la fluorescence. Les valeurs pour le fluorure du sérium, mesurées avec ce réactif après diffusion à température ordinaire, sont en accord avec celles obtenues avec l'électrode à fluorure et avec celles prédites par la clearance rénale du fluorure radioactif. L'écart type relatif lorsqu'on mesure le fluorure $10^{-6}M$ dans 2 ml de sérum est de ±10%.

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INORGANIC POLAROGRAPHY IN ORGANIC SOLVENTS—IV*

POLAROGRAPHY OF METAL OXINATE COMPLEXES IN VARIOUS SOLVENTS

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Summary—The polarograhy of 24 metal oxinate complexes extracted into chloroform, IBMK, and ethyl acetate has been investigated, a methanolic solution of lithium chloride being used as base electrolyte. Only 15 complexes gave rise to reduction waves, and interference-free determinations have been developed for indium and thallium(III) in chloroform, and for bismuth, molybdenum and uranium in IBMK. The use of ethyl acetate offered no special advantages, and was the least selective of the three solvents used.

THE ADVANTAGES associated with a polarographic examination of an organic phase following solvent extraction have been illustrated in previous communications in this series with reference to both ion-association[1,2] and chelate[3] extraction systems. This method of analysis provides a solution of standard composition enabling polarographic waves to be identified easily and used for quantitative analysis.

The extraction system examined not only extends the range of application of this technique, but also provides some fundamental knowledge concerning the polarographic behaviour of 8-hydroxyquinoline (oxine) complexes in organic solvents of low dielectric constant. The only related polarographic examination known to us is the study of copper and palladium oxine complexes in acetic acid solution,[4] but the conditions used for it were not typical of those which prevail following the normal solvent extraction of complexes into organic solvents for the purpose of analysis.

EXPERIMENTAL

Apparatus

An Elliot Polarographic Model 200 was used with a dropping mercury electrode. The following operating conditions were used: potential sweep 0·005 V/sec, drop time 3·4 sec, height of mercury reservoir 60 cm, mercury flow-rate 2·264 mg/sec, temperature 18° (approx.), no damping or countercurrent. An internal mercury pool anode was used and a mercury seal was used to prevent reabsorption of oxygen. Deoxygenation was achieved by bubbling oxygen-free nitrogen through a 5-ml sample for not less than 2 min.

Reagents

8-Hydroxyquinoline, 0·1*M*, in chloroform, isobutyl methyl ketone (IBMK) or ethyl acetate.
Metal ion solutions, $10^{-3}M$.
Potassium perchlorate, 1*M*.
Lithium chloride, 0·5*M* in methanol.

Extractions

Equal volumes (15 ml) of 0·1*M* 8-hydroxyquinoline solution and an aqueous solution containing 2 ml of $10^{-3}M$ metal ion solution, 5 ml of $10^{-3}M$ acidic aqueous oxine solution (to prevent

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* Part III—*Talanta*, 1967, **14**, 715.

precipitation of metal hydroxides) and 1 ml of 1M potassium perchlorate to give a constant ionic strength, were shaken together. The pH was controlled by the addition of sodium hydroxide or perchloric acid, and checked with a pH meter. After equilibration (*ca.* 1 min), the two phases were allowed to separate. The organic phase was then transferred to a 25-ml standard flask, containing 5 ml of 0·5M lithium chloride in methanol, and diluted to volume with methanol. A 5-ml portion was transferred to the polarographic cell containing about 5 ml of mercury as anode-pool, and deoxygenated. Polarograms were recorded at an instrument sensitivity of 4 μA full-scale deflection, over the available potential range.

RESULTS

The half-wave potentials of the polarographic waves observed in IBMK, chloroform, and ethyl acetate are listed in Table I. The aqueous phase was examined before the extraction, but only the lead and tin(II) complexes produced polarographic waves, at −0·32 and −0·4 V respectively.

Table I.—Polarographic behaviour of some metal–oxine complexes

Metal ion	Aqueous phase, pH	$E_{1/2}$ *vs.* Hg pool, V		
		IBMK	chloroform	ethyl acetate
—*	7	−1·0	−0·8	−1·2
†		−1·5	−0·8	−2·0
Be	8	—	—	—
Bi	6	−0·01	−0·41	−0·36
Cd	8	—	—	—
Ce	10	—	—	ppte
Co(II)	8	—	—	0·76
Cu(II)	4	−0·19	−0·33	−0·33
Ga	8	—	—	−0·7
Fe(III)	4	ppte	−0·3	−0·24
In	7	—	−0·1	−0·3
Mn(II)	8	—	—	ppte
Mo(VI)	2	−0·3	−0·46	−0·3
Nb(V)	6	ppte	ppte	ppte
Ni	5	−0·77	—	−0·76
Pb	8	−0·35	—	−0·33, −0·67
Pd	8	−0·18, −0·73	−0·6, −0·75	−0·21, −0·66
Sn(II)	3	—	—	−0·64
Sn(IV)	3	−0·94	—	−0·74
Ti(IV)	4	—	—	−0·82
Tl(III)	7	—	−0·3	—
U(VI)	7	−0.43	−0.55	−0.47
V(V)	4	—	—	—
W(VI)	3	—	—	—
Zn	4	—	—	—
Zr	2	—	—	—

* Solution containing all reagents used, but no metal ion.

† In absence of oxine.

Elements which do not normally give well-defined polarographic waves in aqueous solution, *e.g.*, silver, beryllium, magnesium, niobium and thorium, but which are extracted appreciably by 8-hydroxyquinoline in organic solvents[5] were also examined. However, in no instance was a reduction wave observed in the organic phase. Thallium(I) was not examined because it is not quantitatively extracted by this reagent.

Although chloroform is the most widely used solvent for oxinate complexes the somewhat limited potential range available with it prompted the examination of IBMK and ethyl acetate. It is not very surprising that some of the reduction waves noticed in chloroform are not observed in the other solvents, probably because of less efficient extraction, *e.g.*, thallium(III). It is also not surprising that the additional waves observed in IBMK and ethyl acetate are those of species with reduction potentials beyond the range of chloroform, *e.g.*, tin(IV) and titanium(IV). However, it is difficult to account for the appearance of the reduction waves for cobalt(II), gallium, tin(II) and tin(IV) in ethyl acetate, nickel and lead in IBMK and ethyl acetate, and the disappearance of the indium reduction wave in IBMK.

Analytical determinations following selective solvent extraction are often based on colorimetric methods, involving either direct measurement of the amount of the metal chelate in the organic phase or, if more sensitivity is required, back-extraction into an aqueous phase, which is often followed by destruction of the 8-hydroxyquinoline present and development of a more sensitive colour with some other reagent. Such methods are, however, time-consuming and it is often very difficult to destroy the 8-hydroxyquinoline.[6] In addition, even with accurate pH control and the use of masking agents it is not always possible to obtain a sufficiently selective extraction. This is particularly evident in the fluorescence determination of oxinate complexes of aluminium, gallium, indium, *etc.*

One major analytical technique capable of dealing directly with the organic phase is atomic-absorption spectroscopy, but this does not permit sequential analysis in the true sense, as does polarography.

In the chloroform phase (Table I) reduction waves of only 8 of the 24 species examined are observed, *viz.*, bismuth, copper(II), iron(III), indium, molybdenum(VI), palladium, thallium(III) and uranium(VI), and of these only indium and thallium(III) have been further investigated because neither produces waves in the other two solvents studied. The species bismuth, molybdenum(VI) and uranium(VI) have been studied in more detail in IBMK; copper(II), iron(III), nickel and lead were not subjected to further investigation because of the abundance of analytical methods already available. Palladium was not examined in detail because it was only extracted very slowly and the ethyl acetate system was ignored because it was the least selective and gave additional waves only for cobalt and for gallium.

Chloroform extraction of indium and thallium

Linear calibration curves for both indium and thallium(III) were obtained over the range 1–100 ppm. The range could presumably be extended by using the extraction system as a means of concentration.[3] The extraction procedure used was the same as that described above at pH values between 4 and 9. A plot of log $i/(i_d - i)$ *vs.* E were linear for the indium and thallium(III) waves, with slopes giving values of n (no. of electrons in electrode reaction) of 1·48 and 1·77 respectively.

The indium reduction wave is sufficiently positive, in comparison with the other co-extracted ions, *i.e.*, bismuth, copper(II), iron(III), molybdenum(VI), palladium, thallium(III) and uranium(VI), for there not to be any severe interference. However, very large excesses of other ions are undesirable because they will certainly consume reagent, possibly at the expense of indium. In this event, the following masking scheme was found to be effective in eliminating the extraction and thus the interference of 50-fold molar excesses of these ions.

(*i*) Extraction at pH 5 in presence of potassium cyanide masks to a considerable extent the extraction of copper(II), iron(III), molybdenum(VI) and palladium and partly that of bismuth. The extraction of indium, thallium(III) and uranium(VI) remains totally unaffected.

(*ii*) Extraction at pH 5 with added cyanide and oxalate completely prevents the extraction of bismuth, copper(II), iron(III) and uranium(VI).

(*iii*) If the organic phase remaining after (*ii*) is washed with an aqueous solution of sodium sulphite, thallium(III) is back-extracted and a wash with an EDTA solution at pH 12 was found to remove the last traces of molybdenum(VI) and palladium.

For the determination of thallium the first two steps of this masking scheme should be used, but phosphate should be added as well in step (*ii*) to prevent extraction of indium, and the final solution should be scrubbed with EDTA at pH 12 to remove traces of molybdenum(VI) and palladium.

In neither extraction can EDTA be used as a mass masking agent, because it prevents the extraction of indium and thallium(III) oxinates under almost all conditions.

IBMK extraction of bismuth, molybdenum and uranium

A similar extraction procedure was again used at pH 4–9 for bismuth, pH 1–5 for molybdenum(VI) and pH 5–9 for uranium(VI), and linear calibration curves were obtained over the range 1–100 ppm. Plots of log $i/(i_a - i)$ *vs.* E were linear with slopes giving values of n for bismuth 1·10, molybdenum(VI) 0·88, and uranium (VI) 0·88.

The possible interfering ions are bismuth, copper(II), molybdenum(VI), nickel, lead, palladium, tin(IV) and uranium(VI).

For the determination of bismuth the following masking scheme was found to be effective, although the half-wave potential of its reduction wave is such that other elements need not be completely eliminated.

(*i*) Extraction at pH 4 leaves lead in the aqueous phase.

(*ii*) Extraction at pH 4 in presence of ascorbic acid completely masks copper(II) and partially masks palladium.

(*iii*) Extraction at pH 4 plus ascorbic acid and potassium cyanide masks copper(II), palladium and nickel.

(*iv*) Extraction as in (*iii*) plus tartrate also prevents extraction of uranium(VI).

Under these conditions only bismuth and molybdenum are extracted. It was not found possible to mask the extraction of molybdenum completely, even by back-extraction into an aqueous phase at pH>8 [(Mo(VI)-oxinate is said[5] not to be extracted into chloroform at pH $\gg$ 8]. The only method capable of eliminating molybdenum is to extract initially at pH > 8. It would then be necessary to back-extract into an aqueous phase those other ions likely to interfere. However, the separation of the bismuth and molybdenum(VI) reduction waves (−0·01 and −0·3 V respectively *vs.* mercury- pool anode) is sufficient to allow the determination of bismuth in the presence of quite large quantities of molybdenum. The following simple masking procedure depends almost entirely on the high extractability of the molybdenum(VI)-8-hydroxyquinoline complex and can be used for the determination of molybdenum.

(*i*) Extraction at pH 1 masks the extraction of all ions except molybdenum(VI) and a small quantity of palladium (slow extraction).

(*ii*) Extraction at pH 1 in presence of EDTA allows only molybdenum(VI) to be extracted.

Again, for the determination of uranium it is necessary to mask the extraction of those other ions which are extracted and give rise to polarographic waves. The following masking procedure proved to be effective.

(*i*) Extraction at pH 7 in presence of potassium cyanide completely masks copper(II) and nickel and partly molybdenum(VI).

(*ii*) Extraction at pH 7 in presence of cyanide and EDTA prevents extraction of copper(II), nickel, molybdenum(VI), bismuth, lead and palladium.

In none of these instances was tin(IV) considered, because of its facile reduction to tin(II) which does not give rise to a reduction wave.

Conclusions

The organic reagent 8-hydroxyquinoline reacts with about 45 metal ions. In consequence its use in analytical chemistry is restricted unless the final method of measurement is relatively selective. Even with the use of masking agents, it is not always possible to achieve a sufficiently selective separation, *e.g.*, indium and gallium. These complexes give rise to almost identical maximum wavelengths of absorption and emission and hence spectrophotometry and spectrofluorimetry are of little use in distinguishing between them. A similar situation might occur with mixtures of other elements.

Direct polarographic examination of the organic phase following solvent extraction has been shown to eliminate a number of problems because it does not necessarily require a very selective extraction or the use of a particular solvent. In addition it offers a sensitive method of determination, particularly if the extraction system is used as a means of concentration.

Zusammenfassung—Das polarographische Verhalten von 24 in Chloroform, IBMK und Äthylacetat extrahierten Metalloxinaten wurde mit einer methanolischen Lösung von Lithiumchlorid als Leitelektrolyt untersucht. Nur 15 Komplexe riefen Reduktionsstufen hervor; störungsfreie Bestimmungsmethoden wurden entwickelt für Indium und Thallium(III) in Chloroform sowie für Wismut, Molybdän und Uran in IBMK. Äthylacetat hat keine besonderen Vorteile und war unter den drei verwendeten Lösungsmitteln das wenigsten selektive.

Résumé—On a étudié la polarographie de 24 complexes métalliques de l'oxine extraits en chloroforme, méthylisobutylcétone et acétate d'éthyle, une solution méthanolique de chlorure de lithium étant utilisée comme électrolyte de base. Seulement 15 complexes engendrent des vagues de réduction, et l'on a élaboré des dosages exempts d'interférences pour l'indium et le thallium(III) en chloroforme, et pour le bismuth, le molybdène et l'uranium en méthylisobutylcétone. L'emploi d'acétate d'éthyle n'a pas offert d'avantages spéciaux et il a été le moins sélectif des trois solvants utilisés.

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COMPLEXES MIXTES DES NITRILOTRIACETATES METALLIQUES AVEC L'ACIDE GLUTAMIQUE OU AVEC L'ACIDE ASPARTIQUE

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Résumé—Les nitrilotriacetates métalliques réagissent avec l'acide glutamique et avec l'acide aspartique en formant des complexes mixtes. On a déterminé la constante de formation de ces complexes mixtes.

LA RÉACTION des nitrilotriacétates métalliques avec la glycine, la serine et l'arginine a été étudiée dans ce laboratoire.[1,2] Quelques complexes mixtes de la sérine ont été étudiés récemment.[3] Jusqu'à présent aucun complexe mixte de l'acide glutamique et de l'acide aspartique n'a été signalé dans la littérature. Dans ce travail nous avons étudié la réaction des nitrilotriacétates métalliques avec l'acide glutamique et avec l'acide aspartique.

PARTIE EXPERIMENTALE

Nous utilisons des solutions de perchlorates métalliques qui sont étalonnées par des méthodes complexométriques.[4,5] On emploie l'acide glutamique L et l'acide aspartique DL, tous les deux produits de la firme BDH.

L'électrode de calomel du pH mètre "Radiometer Model 26" est reliée à la solution par un pont Fisher 13-639-55, rempli d'une solution de $NaNO_3$, 0·5*M*.

Les titrages pH-métriques sont effectués à une force ionique de 0·1 maintenue constante par $NaClO_4$ et à la température de 25°.

RESULTATS

Sur la Fig. 1 nous montrons le titrage d'un mélange équimoléculaire de perchlorate de nickel de nitrilotriacétate disodique et d'acide glutamique. Soit "*a*" le nombre de moles de base ajouté pour une mole de métal. Sur la Fig. 1 on observe qu'il y a deux points d'inflexion situés respectivement à $a = 2$ et $a = 3$. Jusqu'à $a = 2$ on titre le proton qui provient du nitrilotriacétate disodique et le proton qui provient du groupe carboxyle ∂ de l'acide aminé (H_2L). En cette région on forme le complexe simple MeX^-.

Entre $a = 2$ et $a = 3$ on titre l'autre proton de l'acide aminé qui est normalement lié au groupe NH_2. Dans cette région de titrage on forme le complexe mixte MeXL. Des résultats similaires sont obtenus avec Cu(II), Co(II), Zn(II), Mn(II) et également quand on utilise l'acide aspartique à la place de l'acide glutamique. Pour Cu(II), Co(II) et Ni(II) nous avons étudié aussi la composition des complexes mixtes par la méthode des variations continues.[6,7] Dans la Fig. 2 nous montrons les courbes obtenues pour le système cuivre–nitrilotriacétate–glutamate. Sur cette Fig. on voit clairement que le complexe mixte contient le métal, le nitrilotriacétate et l'acide aminé dans la proportion 1:1:1.

Etant donné que le complexe simple et le complexe mixte se forment suivant deux étapes distinctes, nous calculons la constante de formation des complexes mixtes en

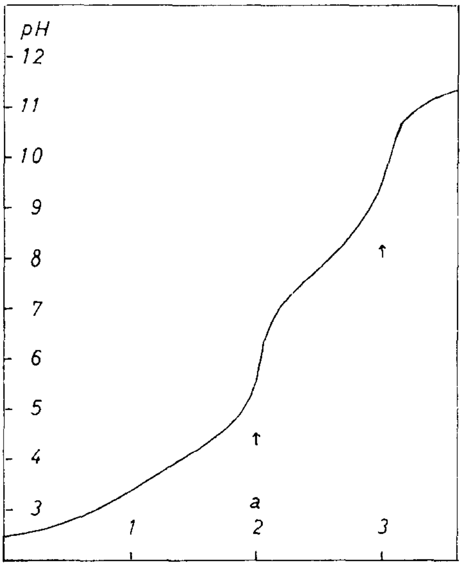

Fig. 1.—Titration par la soude d'un mélange contenant perchlorate de nickel 0·01M en présence de nitrilotriacétate disodique 0·01M et d'acide glutamique 0·01M. "a" représente le nombre de moles de soude ajouté pour une mole de nickel. La force ionique de la solution est maintenue a 0·1 avec l'aide du $NaClO_4$.

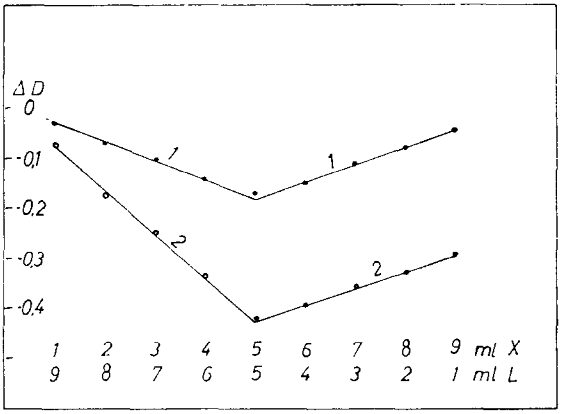

Fig. 2.—Courbes des variations continues pour le système Cu(II), nitrilotriacétate (X) et glutamate (L).
Composition de la solution: 5 ml Cu 0·1M + x ml X 0·1M + (10-x) ml L 0·1M + 35 ml H_2O; pH = 8. La courbe 1 a été mesuré à λ = 620 mμ et la courbe 2 a été mesuré a λ = 850 mμ.

utilisant la portion de la courbe de titrage située entre $a = 2$ et $a = 3$. Selon la notation de Martell[8] les équations suivantes sont valables dans cette dernière région:

$$C_{Me} = C_L = C_X \tag{1}$$

$$C_{Me} = [MeX] + [MeXL] \tag{2}$$

$$C_L = [H_2L] + [HL] + [L] + [MeXL] \tag{3}$$

$$(3 - a)C_{Me} = 2[H_2L] + [HL] + [H] - [OH] \tag{4}$$

$$K_1 = \frac{[H][L]}{[HL]} \qquad K_{12} = \frac{[H][HL]}{[H_2L]} \tag{5}$$

$$K_f = \frac{[MeXL]}{[MeX][L]} \tag{6}$$

Les valeurs de K_1 et K_{12} sont redéterminées et l'on trouve: pour l'acide glutamique $K_1 = 3{,}16 \cdot 10^{-10}$ et $K_{12} = 7{,}4 \cdot 10^{-5}$; pour l'acide aspartique $K_1 = 2{,}52 \cdot 10^{-10}$ et $K_{12} = 2{,}05 \cdot 10^{-4}$. Ces valeurs se comparent bien à celles trouvées dans la littérature.[9]

L'équation (4) conduit à l'équation:

$$[L] = \frac{(3 - a)C_{Me} - [H] + [OH]}{\dfrac{[H]}{K_1} + \dfrac{2[H]^2}{K_1K_{12}}} \tag{7}$$

Avec l'aide des équations (2) et (3), l'équation devient:

$$K_f[L] + 1 = \frac{C_{Me}}{[L]\left\{1 + \dfrac{[H]}{K_1} + \dfrac{[H]^2}{K_1K_{12}}\right\}} = y \tag{8}$$

Un graphique de y en fonction de [L] donne une droite dont la pente est K_f et l'ordonnée à l'origine est 1. Les constantes K_f ne dépendent pas de la concentration initiale des réactifs qui varie entre $4 \cdot 10^{-3}M$ et $2 \cdot 10^{-2}M$. La constante de formation K_f des complexes est donnée dans le Tableau 1.

TABLEAU I.—CONSTANTES DE FORMATION DES COMPLEXES MIXTES MeXL

Me	L = glutamate log K_f	L = aspartate log K_f
Cu(II)	5,10 ± 0,03	5,31 ± 0,02
Ni(II)	4,04 ± 0,03	4,20 ± 0,03
Co(II)	2,96 ± 0,03	3,21 ± 0,03
Zn(II)	2,96 ± 0,04	3,24 ± 0,03
Mn(II)	2,22 ± 0,04	2,08 ± 0,04

DISCUSSION

Les constantes de formation de complexes mixtes suivent la série de stabilité de Irving-Williams.[10] On observe aussi qu'il n'y a pas grande différence entre la stabilité de complexes mixtes dérivant de l'acide glutamique et ceux dérivant de l'acide aspartique. Les complexes mixtes de l'acide aspartique sont un peu plus stables que les complexes mixtes de l'acide glutamique, parceque l'acide aspartique est un peu plus basique que l'acide glutamique.

Il faut noter que les constantes de formation des complexes étudiés dans ce travail sont très proches de celles des complexes mixtes de la glycine, de la sérine et de l'arginine.[1,2]

Soit K_{MeX} la constante de formation du complexe MeX et K_1 la constante de formation du MeL. Evidemment la constante de stabilité globale du complexe mixte K_s est égale à $K_{MeX}K_f$.

Nous avons trouvé empiriquement que, pour les complexes mixtes, la relation suivante est valable:

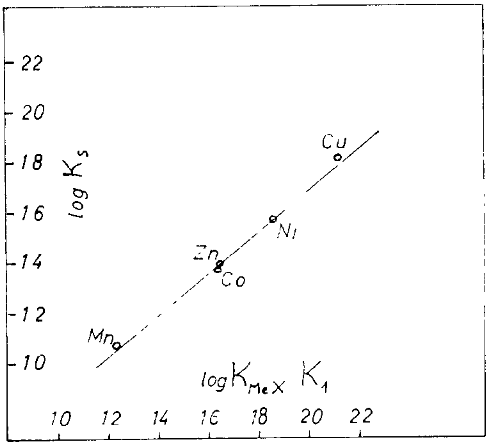

FIG. 3.—Log K_s en fonction du log K_{MeX} K_1, pour les complexes mixtes de l'acide aspartique.

$$\log K_s = \alpha \log K_{MeX}K_1 + C$$

Sur la Figure 3 nous représentons cette relation pour les complexes mixtes de l'acide aspartique. Les constantes K_{MeX} et K_1 sont empruntées à la littérature.[9]

CONCLUSION

Il nous semble que la constante de formation des complexes mixtes qui se forment suivant la réaction des nitrilotriacétates métalliques avec des acides aminés est principalement influencée par le groupe carboxyle et le groupement α-amino, le reste de la molécule de l'acide aminé n'ayant que peu d'influence.

Zusammenfassung—Metallnitrilotriacetate reagieren mit Asparagin- und Glutamin-säure und bilden mit diesen gemischte Komplexe. Die Bildungskonstanten der Komplexe wurden bestimmt.

Summary—The metallic nitrilotriacetates react with aspartic acid and glutamic acid and form with them mixed complexes. The formation constants of these complexes were determined.

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POTENTIOMETRIC STUDIES ON THE FORMATION OF METAL COMPLEXES WITH *TRANS*-1,2-DIAMINOCYCLOHEXANE-*N*,*N*,*N'*,*N'*-TETRA-ACETIC ACID—I

PROTONATION OF THE LIGAND

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Summary—The protonation of *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetra-acetic acid is studied potentiometrically with the hydrogen electrode. The formation constants have been re-evaluated at 25·0° at an ionic strength of 3·0 ($NaClO_4$), with a least-squares treatment of the data. The potentiometric data are explained from the law of mass action, using a model which assumes five different ligands to be present in the solution; the logarithmic stepwise stability constants are then 9·90, 6·72, 3·65 and 3·21 for the mono-, di-, tri- and tetra-protonated ligand respectively.

IN THIS laboratory, investigations on the formation of metal complexes with different polyaminepolycarboxylic acids are of great interest. Among these, chelates with *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetra-acetic acid are among the compounds especially studied.

As this ligand is partly dissociated in aqueous solution, a proper knowledge of its behaviour is of fundamental importance in the study of complex formation. In the evaluation of stability constants of metal chelates, the protonation constants are parameters in the calculations. Thus it is essential to know these most accurately. The dissociation constants have previously been reported from several independent laboratories (Table I) and differ greatly from one laboratory to another. It therefore seemed desirable to make a very careful study of the dissociation properties of this compound. In the present investigation, models have been sought which give the best explanation of the potentiometric results. This is done in two ways: the potentials of the solution and the corresponding model solution are made identical for each experimental point and the difference in the amount of base added to each solution is considered, or the amounts of base added are made equal and the difference in potentials is considered.

EXPERIMENTAL

Apparatus

The potentials were measured with the Dynamco digital voltmeter 2022 (Dynamco Instruments Limited, Surrey, England), measured after stabilization to within 0·1 mV. The Metrohm Coulometer E-211 (Metrohm AG., Herisau, Switzerland) was used as a source of constant current (±0·1 %). Timing was by counting the impulses from an oscillating circuit.

TABLE I.—DISSOCIATION CONSTANTS OF *trans*-1,2-DIAMINOCYCLOHEXANE-*N*,*N*,*N'*,*N'*-TETRA-ACETIC ACID (H_4X)

Ref.	Method	Medium and temp.	Logarithmic formation constants*				Reported accuracy
			k_1	k_2	k_3	k_4	
1	Hydrogen electrode	0·1*M* KCl, 20°C	11·70	6·12	3·52	2·43	—
2	—	—	10·80	7·56	3·3	2·4	—
3,4	Solubility	$\mu = 0$ 20°C	—	—	1·92	0·96	—
5	Glass electrode	0·1*M* KNO_3, 25·3°C	10·76	6·13	—	—	—
6	Glass electrode	0·1*M* KNO_3, 25°C	11·58	6·12	3·55	2·40	—
7	Spectrophotometry	0·1*M* KNO_3, 20°C	12·3	—	—	—	±0·25
†	Glass electrode	1*M* $NaClO_4$, 20°L	8·85	6·48	2·3	2·2	±(0·02–0·05)

* $k_1 = [HX^{3-}]/[H^+][X^{4-}]$; $k_2 = [H_2X^{2-}]/[H^+][HX^{3-}]$ *etc.*

† G. Anderegg, *Helv. Chim. Acta.* 1967, **50**, 2333 (added in proof).

Reagents

The *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetra-acetic acid (DCTA) was reagent-grade quality from Fluka and was used without further purification.

The perchloric acid *p.a.* was obtained from Riedelde Haën, Hannover, Germany, and the sodium perchlorate *p.a.* from Fluka. The hydrogen was made oxygen-free by passing it through a hot copper column.

Method

The protonation was studied by means of the following electrode system:
Ag/Ag$^+$ (0·01*M*), ClO_4^-(3*M*), Na$^+$(2·99 mM)/$NaClO_4$(3*M*)/experimental solution/Pt (H_2).
The base added was internally generated electrolytically by means of a separate electrode system: Ag/Ag$^+$(0·1*M*), ClO_4^-(3*M*), Na$^+$(2·9*M*)/ $NaClO_4$(3*M*)/experimental solution/Pt.
Both electrode systems were designed as described by Forsling *et al.*[8]

TABLE II.—DISSOCIATION CONSTANTS FOR DCTA, AND THE IONIC PRODUCT FOR WATER (3·00*M* $NaClO_4$, 25·00°C)

Reaction	Equation 1 minimized		Equation 4 minimized	
	log *k*	Standard deviation	log *k*	Standard deviation
$H_2O = H^+ + OH^-$	−14·48	0·01	−14·52	0·03
$H^+ + X^{4-} = HX^{3-}$	9·91	0·01	9·88	0·02
$H^+ + HX^{3-} = H_2X^{2-}$	6·72	0·01	6·72	0·01
$H^+ + H_2X^{2-} = H_3X^-$	3·61	0·02	3·69	0·02
$H^+ + HX^- = H_4X$	3·23	0·03	3·19	0·05

E^0 for the hydrogen electrode used was found to be −0·644 V (s.d. 0·0003 V) for equation 1 and −0·642 V (s.d. 0·0005 V) for equation 4.

To avoid the presence of oxygen and carbon dioxide, hydrogen gas was bubbled through the cell, as well as being passed to the Pt(H_2) electrode; this also gave satisfactory stirring.

The titrations always started from acid solution, the cell being connected as cathode in the coulometric circuit. This was preferred in order to eliminate the presence of carbonate.

The normal potential of the hydrogen electrode (E^0) was determined from Gran plots[9] of results from separate coulometric titrations. The experimental solution was 2·999*M* sodium perchlorate with 0·001*M* perchloric acid. The concentration of the perchloric acid was found from Gran plots. This titration was performed over the pH range 2–11, and the ionic product of water could be determined. The results are given in Table II.

A titration curve of 0·001*M* DCTA in 3·0*M* sodium perchlorate is shown in Fig. 1. This curve has—as expected—two inflections, after the addition of two and three equivalents of base, indicating the possible existence of a di- and a tri-protonated compound in solution. Any other simple and direct conclusions might be of questionable validity.

Interpretation of the results

The Algol version of the least-squares computer programme Letagrop[10] was kindly supplied by L. G. Sillén. This programme was modified for our computer (Univac 1107) to give sufficiently short computing time, because the potentiometric data resulted in numbers of very different orders of magnitude. The computing was started by estimating the dissociation constants published by Schwarzenbach and Ackermann,[1] slightly modified in accordance with the titration curve obtained in this work. After a few successive refinements, some corrections for systematic errors owing to small impurities in the sodium perchlorate and to inaccuracy in the normal potential were made, before the refinement of evaluation of the dissociation constants and of the ionic product of water could be continued.

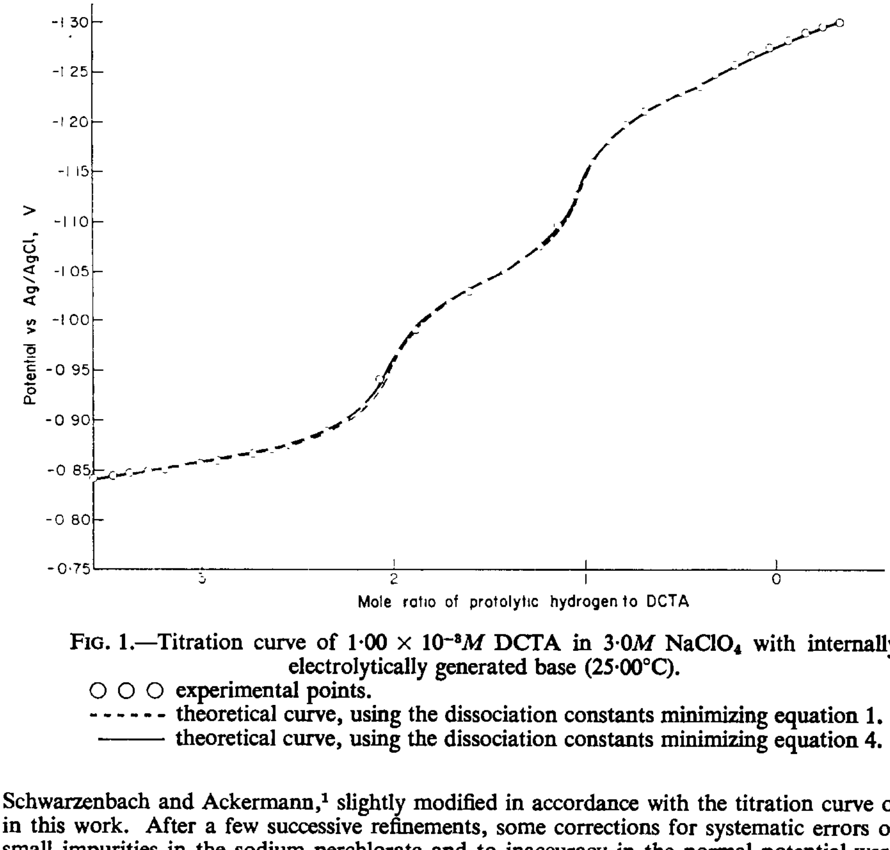

FIG. 1.—Titration curve of 1·00 × 10^{-3}*M* DCTA in 3·0*M* $NaClO_4$ with internally electrolytically generated base (25·00°C).

O O O experimental points.

- - - - - - theoretical curve, using the dissociation constants minimizing equation 1.

——— theoretical curve, using the dissociation constants minimizing equation 4.

The square-error sum to be minimized in the calculation was first chosen to be

$$U_1 = \Sigma(H_{calc} - H_{exp})^2 \tag{1}$$

where H_{exp} is the tota lconcentration of protolytic hydrogen calculated from the concentrations of the various compounds in the solution and H_{calc} is obtained from the equations

$$H_{calc} = [H^+] + \Sigma_i H_i X \tag{2}$$

$$\log [H^+] = \frac{E - E^0}{0{\cdot}05915} \tag{3}$$

together with sufficient mass-action equilibrium equations to describe the system.

Afterwards, the calculations were repeated by defining the square-error sum according to the equation

$$U_2 = \Sigma(E_{\text{calc}} - E_{\text{exp}})^2 \tag{4}$$

where E_{exp} is the measured potential (in volts) *vs.* the reference electrode system. A Newton-Raphson procedure was used to determine the calculated potential (E_{calc}), making $H_{\text{calc}} - H_{\text{exp}} = 0$.

Even with use of the computing method to vary the complex-formation parameters along the main axes of the pit,[10] it was found desirable to describe the system by the law of mass action in such a way that the co-variations of the parameters were made as small as possible. This was best done by describing the system with stepwise dissociation constants together with the ionic product of water.

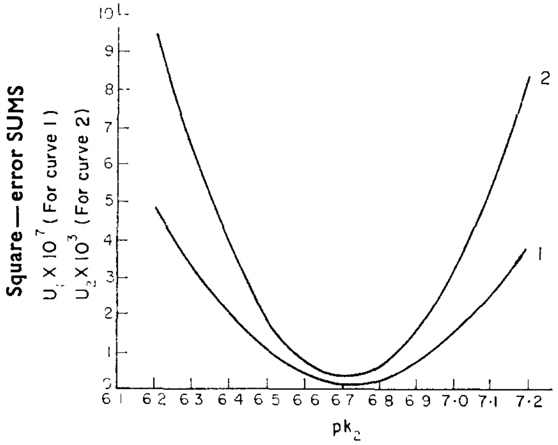

FIG. 2.—The influence of the dissociation constant k_2 on the square-error sums U_1 (curve 1) and U_2 (curve 2). The remaining dissociations and the ionic product of water are taken at the minima.

Because of the logarithmic nature of potentiometric measurements, the logarithmic values of these assumed constants were used as basic points during their systematic variation to obtain favourable error distributions.

The calculated stepwise stability constants minimizing equation 1 were used as initial values for further refinements using equation 4. This resulted in the detection of a serious mistake in the previous calculations, that resulted from having reached an inflection instead of a minimum. To avoid further mistakes, successive refinements were initially made by alternately minimizing equation 1 and equation 4, followed by finding the two sets of minimizing parameters.

Table II shows the computed constants for the various dissociated species in the solution at the minimum, from equations 1 and 4. There are apparently good reasons for introducing five species ranging from unprotonated to tetraprotonated to explain the experimental data, as the introduction of all these compounds and the ionic product of water resulted in significant lowering of both square-error sums (U_1 and U_2). As an example, the square-error sums at different pk_2 values are shown in Fig. 2.

DISCUSSION

Because of the low solubility of the reagent, it has only been studied in concentrations of 0·001*M*. Thus the data do not make it possible to determine the existence of polymeric products (*e.g.*, HX_2 *etc.*) The high ionic strength (3·0*M* sodium perchlorate) used means that the dissociation values cannot be compared with the previously published values, but it also ensures that errors due to ionic strength effects are kept very slight, even in the very strongly acidic and alkaline solutions which had to be used, because the ionic strength is then essentially dependent only on the concentration of the inert salt added. The use of the hydrogen electrode instead of the more common glass electrode was preferred to ensure reliable results.

The dissociation constants are chosen to minimize the square-error sum of the measured parameters, giving all the experimental points equal weight. As a very wide concentration range is covered, it is highly probable that the way the square-error sum is defined influences the dissociation constants which minimize it. Table II shows that this will result in only some slightly different constants when the error in potential or in the amount of the acid present is minimized. It is assumed that the use of two minimizing functions will greatly increase the likelihood of achieving the lowest minimum instead of an erroneous one.

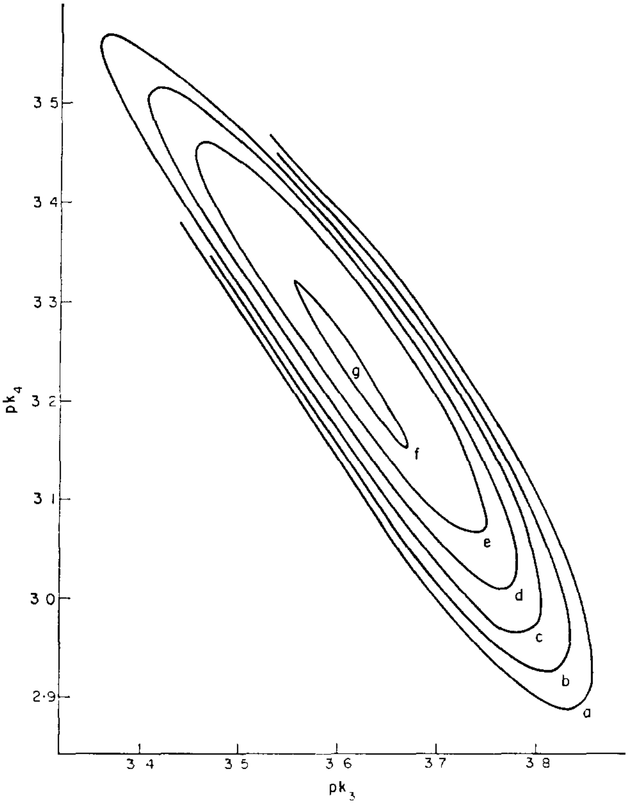

FIG. 3.—Graphical representation of the effect of co-variance of the dissociation constants k_3 and k_4 on the square-error sum. This sum is indicated by the contours. Curve *a*: $U = 7{\cdot}0 \times 10^{-8}$, curve *b*: $U = 6{\cdot}0 \times 10^{-8}$, curve *c*: $U = 5{\cdot}0 \times 10^{-8}$, curve *d*: $U = 4{\cdot}0 \times 10^{-8}$, curve *e*: $U = 3{\cdot}0 \times 10^{-8}$, curve *f*: $U = 1{\cdot}5 \times 10^{-8}$ and point *g*: $U = 1{\cdot}4 \times 10^{-8}$ (minimum)

As pointed out by various authors,[11,12] great care has to be taken in treating successive complexes with approximately equal dissociation constants, as misleading conclusions are easily drawn. Therefore a more thorough examination of the triprotonated and the tetraprotonated compound was made by calculating the square-error sum with variously combined values of the two corresponding dissociation constants. The results are given in Fig. 3, which shows that the constants presented give the best explanation of the experimental data. The distribution of the various compounds in solution, with different amounts of base generated, is given in Fig. 4.

It is of importance that the dissociation constants are quite independent of the function used in defining them. This makes the constants more suitable for later use.

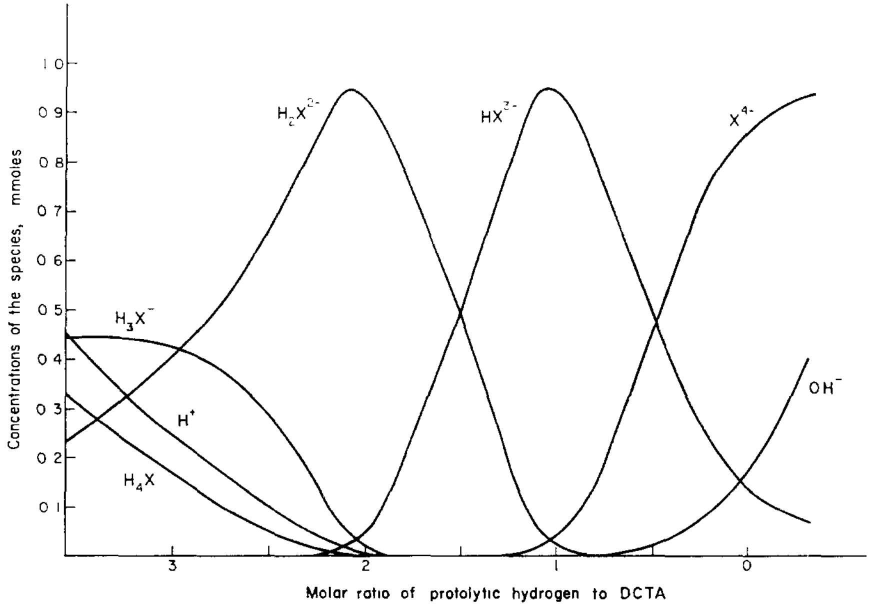

FIG. 4.—Distribution of the species in solution, as a function of acidification, calculated from Table II (equation 1).

The present potentiometric study does not make it possible to study the presence of compounds containing more than four protons bound to the molecule. Such studies require very acid solutions, and this will result in inaccurate measurements. The species X^{4-} seems to be present in very strongly alkaline solution. It is obvious that species with five or more negative charges are not formed, *e.g.*, $X(OH)^{5-}$, but owing to the difficulties in making measurements in such extremely alkaline solutions, this was not verified experimentally.

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Zusammenfassung—Die Protonierung von trans-1,2-Diaminocyclohexan-*N*,*N*,*N'*,*N'*-tetraessigsäure wurde potentiometrisch mit der Wasserstoffelektrode untersucht. Die Bildungskonstanten wurden bei 25° und einer Ionenstärke von 3,0 ($NaClO_4$) unter Behandlung der Meßdaten nach der Methode der kleinsten Fehlerquadrate neu berechnet. Die potentiometrischen Daten werden mit dem Massenwirkungsgesetz interpretiert, wobei ein Modell verwendet wird, das fünf verschiedene Liganden in der Lösung annimmt. Dann sind die logarithmischen Stabilitätskonstanten für die stufenweise Protonierung 9,90; 6,72; 3,65 und 3,21 für den ein-, zwei-, drei-, bzw. vierfach protonierten Liganden.

Résumé—On a étudié potentiométriquement, avec une électrode d'hydrogène, la protonation de l'acide *trans*-1,2-diaminocyclohexanetétracétique. Les constantes de formation ont été de nouveau évaluées à 25,0° à une force ionique de 3,0 ($NaClO_4$), avec traitement des données par la méthode des moindres carrés. On explique les données potentiométriques à partir de la loi d'action de masses, utilisant un modèle qui admet la présence de cinq ligands différents dans la solution; les constantes de stabilité logarithmiques étagées sont alors 9,90; 6,72; 3,65 et 3,21 pour le ligand mono, di-, tri- et tétraprotoné respectivement.

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ANALYTICAL APPLICATIONS OF HYDROXYCOUMARINS

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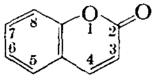
Summary—A review is presented of the analytical potentialities and physico-chemical properties of hydroxycoumarins.

COUMARINS, derivatives of benzo-α-pyrone (I), occur in plants belonging to the natural orders of *Orchidaceae*, *Leguminaceae*, *Rutaceae*, *Umbelliferae* and *Labiatae*.[1]



(I)

Some coumarin derivatives exhibit distinct physiological, photodynamic and bacteriostatic activity.[2-4] Besides application of their physiological activity, a number of uses have been found for them.[5] The chelating characteristics of the coumarins have long been known; 4-methylumbelliferone is a well known fluoresence indicator and the bacteriostatic properties of some of the coumarins have been attributed to chelation.

In the last decade various coumarins have been extensively studied as analytical reagents. Physico-chemical studies of the ligands and the complexes have also been reported.[6] The relative positions of the hydroxy and carbonyl groups have been found to alter the spectral characteristics of the compounds and the reactivity of the hydroxy groups, and the effect of substitution on the absorption spectrum of the parent compound has been studied. The dissociation constants of the various ligands have been determined potentiometrically. The effect of substitution on the basicity of the ligands has been investigated and an attempt made to correlate the basicity of the ligands with the frequency of the hydroxy group absorption bands in the infrared region. A linear relationship between the Hammett σ function for the substituted ligands and the infrared absorption frequency of the hydroxy group has been established.

Methylation studies of *o*-dihydroxycoumarins derived from esculetin and daphnetin show that the hydroxy group at the 7-position can be preferentially methylated, though ordinarily a dimethyl derivative is obtained. It is concluded that the 7-hydroxy group is slightly more reactive than the other but not significantly so. Infrared studies indicate the presence of only weak intramolecular hydrogen bonding.

Coumarins show maximum absorption at about 300 mμ, with log $\epsilon = 4$. The spectrum usually shows additional strong bands between 250 and 340 mμ. The introduction of a hydroxy group into the coumarin molecule modifies its absorption characteristics,[7] generally causing a bathochromic shift of the principal absorption band. This shift due to the auxochromic hydroxy group results from the transition

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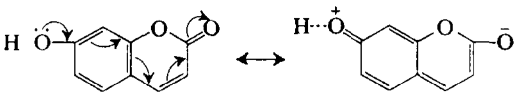
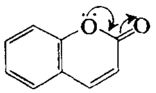
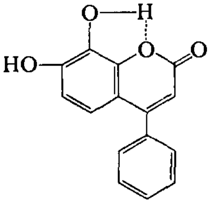
from the ground state to the excited state by an interaction of the type:



which would result in a decrease in transition energy and hence displacement to longer wavelengths. Compounds such as 5,7-dihydroxy-, 6,7-dihydroxy- and 7,8-dihydroxy-coumarins all exhibit bathochromic shifts. The substitution of a hydroxy group at the 8-position results in a significant hypsochromic shift. This is possible because a hydroxy group in this position binds the electron pair of the pyrone oxygen atom, leading to the suppression of the n-π interactions of coumarins as shown in **II**. The substitution of a hydrogen atom by a methyl group[8] either in the benzene ring or in the heterocyclic ring does not produce any significant change in the absorption characteristics of the coumarins. Any hypsochromic effect is attributed mainly to steric hindrance with the hydrogen atom at the *ortho* or *peri* position. A methyl group substituted in the 4-position does not have any marked effect on the spectrum of esculetin but causes a significant hypsochromic shift of the principal absorption band of daphnetin. This shift has been attributed to weakening of the conjugation between the 7-hydroxy group and the lactone carbonyl group.



(II)



(III)

4-Phenylesculetin shows a considerable bathochromic shift as a result of an increase in the number of resonating forms. The phenyl group substituted in the 4-position of daphnetin exhibits a weak electron donor effect, this effect being particularly marked because the electron contribution to the carbonyl group from the heterocyclic oxygen atom is reduced by hydrogen bonding by the 8-hydroxy group (III). As this structure does not involve any increase in conjugation of the carbonyl group, there is no great shift in the principal absorption band.

The inductive and resonance effects due to the substituents on the reacting centre of the ligand can be measured by the magnitude of the Hammett σ function, which covers both effects. The Hammett σ function has been calculated for some coumarins and their derivatives (Table I) and plotted against the infrared frequency for the hydroxy groups. Substitution of a methyl group in esculetin and daphnetin has an electron donating effect; substitution of a phenyl group has the reverse effect. The σ values calculated from the first dissociation constant give a linear relationship with the frequency shifts, but those calculated by use of the second dissociation constant or the overall dissociation constant do not. This shows that only one hydroxy group is affected by substitution in the 4-position. The slopes of the graphs for the esculetin and daphnetin series are of opposite sign.

TABLE I

Compound	pK_1	pK_2	Hammett σ function
Esculetin	7·31	8·03	—
4-Methylesculetin	7·44	8·12	−0·13
4-Phenylesculetin	7·27	8·01	+0·04
Daphnetin	7·32	8·15	—
4-Methyldaphnetin	7·63	8·42	−0·31
4-Phenyldaphnetin	7·40	8·20	−0·08

Apparent stability constants of metal complexes with various *o*-dihydroxycoumarins have been calculated (Table II) and increase with increase in the basic strength, pK_{12}, of the ligand. The greater stability of phenyl -substituted complexes appears to be due to resonance effects, but the values for molybdenum complexes with daphnetins have not yet been explained.

TABLE II

Ligand	pK_{12}	log K for complex			
		Mo	Nb	Ti	U
Esculetin	15·34	3·65	10·43	8·8	3·56
4-Methylesculetin	15·56	7·55	12·07	10·7	4·03
4-Phenylesculetin	15·28	8·20	—	—	4·30
Daphnetin	15·47	8·01	12·94	14·9	3·21
4-Methyldaphnetin	16·05	7·21	13·24	—	4·15
4-Phenyldaphnetin	15·60	7·45	—	—	4·23

The wavelength of maximum absorption for transition metal chelates with dihydroxycoumarins depends on the concentration of ligand, the pH, and the type of solvent. In view of the reducing character of the dihydroxycoumarins, it has been suggested that the metal complexes have charge-transfer spectra.

SYNTHESIS OF COUMARINS

Coumarins, in general, can be synthesized by the Pechmann reaction,[9] *i.e.*, by condensing the appropriate phenolic compound, or its derivative, with malic acid or β-ketonic ester in the presence of concentrated sulphuric acid. The methods used for analytically important hydroxycoumarins are outlined below.

3-Acetyl-4-hydroxycoumarin[10]

Though many methods[11–14] are available for synthesis of 4-hydroxycoumarin and its subsequent acetylation in the 3-position, the one due to Stahmann *et al.*[14] appears to be the best. In this method salicylate is acetylated with acetic anhydride and concentrated sulphuric acid at 40° to yield methyl acetylsalicylate, which is then separated and condensed with sodium in liquid paraffin. The reaction mixture is kept at 250° for about 2 hr and then filtered hot. Acidification and crystallization yield 4-hydroxycoumarin, m.p. 200–206°. The coumarin is then acetylated with acetyl chloride in dry pyridine containing a few drops of piperidine. The mixture is kept at 37° for 48 hr, then poured into ice and dilute hydrochloric acid to yield 3-acetyl-4-hydroxycoumarin. The product, crystallized from aqueous ethanol and then sublimed, melts at 138°.

Oximidobenzotetronic acid[15]

The preparation involves the treatment of 4-hydroxycoumarin with aqueous sodium nitrite solution and subsequent acidification in ice-cold medium. On crystallization from hot chloroform, shining pale yellow crystals of oximidobenzotetronic acid are obtained, m.p. 149° (decomp.).

6,7-Dihydroxycoumarin (esculetin)[16]

An intimate mixture of hydroxyhydroquinone triacetate, malic acid and concentrated sulphuric acid is heated on a boiling water-bath till effervescence ceases. The reaction mixture, after cooling, is poured into crushed ice, stirred and left overnight. Crystallization from dilute alcohol gives esculetin as pale yellow prisms, decomposing above 270°.

4-*Methyl*-6,7-*dihydroxycoumarin* (4-*methylesculetin*)[16]

To an ice-cold solution of hydroxyhydroquinone triacetate in acetoacetic ester, concentrated sulphuric acid is added gradually with stirring, the temperature being kept at 0° for about 1 hr. The deep red viscous product is kept in the refrigerator for 24 hr and then poured, with constant stirring, into water. The resulting solid is filtered off, washed with water, dried, and crystallized from ethanol as yellow needles (m.p. 276–8°).

4-*Phenyl*-6,7-*dihydroxycoumarin* (4-*phenylesculetin*)[17]

A paste of benzoylacetic ester and hydroxyhydroquinone triacetate is added to 75% sulphuric acid and dissolves in it with evolution of heat to form a deep red solution. This solution is heated to 80° on a water-bath for about an hour and is occasionally shaken. After cooling to room temperature it is poured, with stirring, into cold water and the resultant mixture allowed to cool to room temperature. After filtration, the precipitate is washed with cold water till free from acid, and is then dissolved in hot borax solution, whereupon 4-phenylesculetin borate separates. This borate is decomposed with dilute sulphuric acid and the product is crystallized from alcohol as rectangular tablets and tiny prisms, m.p. 267–8°.

7,8-*Dihydroxycoumarin* (*daphnetin*)[9]

An intimate mixture of requisite amounts of pyrogallol, malic acid and concentrated sulphuric acid is heated for about 2 hr on an oil-bath maintained at 120°, till effervescence ceases. The product, after cooling, is poured with stirring into crushed ice and left overnight in the refrigerator. The solid that separates out, after filtration, is crystallized from dilute alcohol; the daphnetin is obtained as pale yellow needles melting at 256–7°.

4-*Methyl*-7,8-*dihydroxycoumarin* (4-*methyldaphnetin*)[18]

To an ice-cold solution of pyrogallol in acetoacetic ester, concentrated sulphuric acid is added gradually with constant stirring, the temperature being kept at 0° for about an hour. The deep red viscous liquid is kept in the refrigerator for about 24 hr and then poured with stirring, into water. The solid which separates is filtered off, washed with water and dried. It is crystallized from benzene as colourless needles melting at 234–5°.

4-*Phenyl*-7,8-*dihydroxycoumarin* (4-*phenyldaphnetin*)[19]

To a cold solution of pyrogallol in benzoylacetic ester, the requisite amount of concentrated sulphuric acid is gradually added with stirring, the temperature being kept at 0°. The deep red viscous product is kept in the refrigerator for about 24 hr and then poured with stirring into water. The solid which separates is filtered off, washed with water and dried. It is crystallized from benzene as colourless needles, m.p. 190–92°.

3-*Phenyl*-7,8-*dihydroxycoumarin* (3-*phenyldaphnetin*)[20]

The compound can be synthesized by the method of Bargellni[21] as modified by Krishnaswamy.[02] Pyrogallol, sodium acetate and acetic anhydride are refluxed for 10 hr, cooled, and poured into water. The acetate which separates out is deacetylated with cold concentrated sulphuric acid. The compound, on crystallization from aqueous alcohol, melts at 213–5°.

3-*Benzyl*-4,5-*dihydroxycoumarin*[22]

An equimolar mixture of resorcinol, ethyl benzyl malonate and diphenyl ether is condensed and the resulting product is treated with petroleum ether. It is then filtered off, washed several times with ether, and crystallized from ethanol, m.p. 259–60°.

ANALYTICAL APPLICATIONS

The applications are summarized in Table III.

Cerium

Cerium(IV)–3-acetyl-4-hydroxycoumarin complex is quantitatively precipitated at pH 4·0–8·5, and as little as 4 mg of cerium has been estimated with this reagent.[23] The complex is usually ignited to CeO_2 and weighed. As the reagent does not form

TABLE III.—ANALYTICAL USES OF HYDROXYCOUMARINS

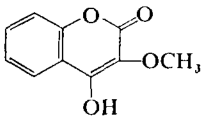
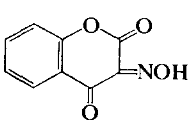
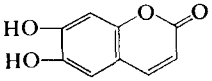
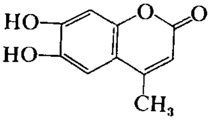
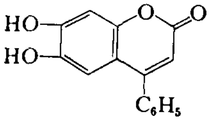
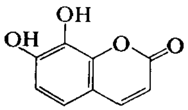
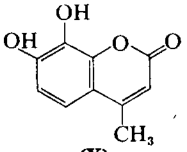
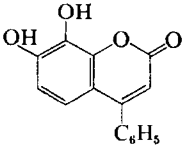
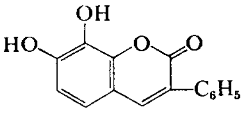
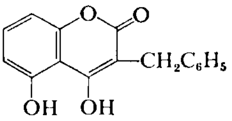
Coumarin	Metal ion determined	Reference
 (IV) 3-Acetyl-4-hydroxycoumarin	Ce(IV) (g) Fe(III) (s) Th(IV) (g), U(VI) (g) Ti(IV) (g), Zr(IV) (g) U(VI) (s)	23 30 44 46 53
 (V) Oximidobenzotetronic acid	Co(II) (s) Co(II) (g) Fe(II) (s) Fe(II) (g) Pd(II) (g) Ru(III) (s), Rh(III) (s) Ir(IV) (s) Os(IV) (s), Pt(IV) (s)	26 27,28 31 32 40 41 42 43
 (VI) Esculetin	Fe(III) (s) Mo(VI) (s) Nb(V) (s) Ti(W) (s)	34 35 39 50
 (VII) 4-Methylesculetin	Mo(VI) (s) Nb(V) (s) Ti(IV) (s)	35 39 50
 (VIII) 4-Phenylesculetin	Mo(VI) (s) Ti(IV) (g), Zr(IV) (g)	35 49
 (IX) Daphnetin	Mo(VI) (s) Ti(IV) (s)	6 51

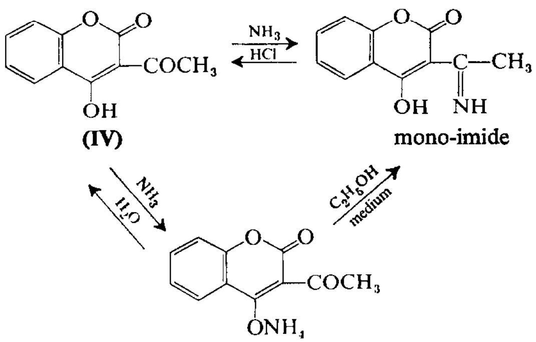
Table (III) *continued*

Coumarin	Metal ion determined	Reference
 (X) 4-Methyldaphnetin	Mo(VI) (s) Nb(V) (g), Ta(V) (g) Th(IV) (g) Ti(IV) (g)	6 38 45 47
 (XI) 4-Phenyldaphnetin	Mo(VI) (s) Nb(V) (g), Ta(V) (g) Ti(IV) (g) Zr(IV) (g)	6 37 48 57
 (XII) 3-Phenyldaphnetin	Mo(VI) (s) U(VI) (s)	36 55
 (XIII) 3-Benzyl-4,5-dihydroxycoumarin	Ti(IV) (s) U(VI) (s)	52 56

(g) gravimetric determination; (s) spectrophotometric determination.

insoluble complexes with the tervalent rare earth metals, it can be used for the separation of cerium(IV) from large quantities of lanthanum, yttrium and gadolinium, *etc.*

An attempt[24] to use the ammonium salt of the reagent (which is soluble in water and thus avoids use of organic solvents) failed because this salt is unstable, tending to lose ammonia and give a mono-imide.



Cobalt

In his monograph,[25] Young has summarized the known methods of determination of cobalt and mentions oximidobenzotetronic acid (V). This coumarin derivative has certain advantages for the spectrophotometric estimation of cobalt.[26] From infrared studies,[24] it appears that the oxime and the 4-carbonyl group take part in chelation, forming a 6-membered ring with the metal ion.

Cobalt forms a deep red complex soluble in water and not extractable into chloroform, ether, n-pentanol, benzene, *etc.* The complex is quite stable and the colour remains constant for at least a week. The absorbance of the complex is maximal and independent of alkalinity at $pH > 10$. The complex has maximum absorption at 485 mμ and obeys the Beer–Lambert law over the range 0–4·7 ppm of cobalt. As little as 0·01 ppm of cobalt can be determined, and Ni(II), Cu(II), Mn(II), Be(II), Zn(II), Al(III), Cr(III), V(V), Mo(VI), W(VI), F^-, Cl^-, Br^-, I^-, CH_3COO^-, SO_4^{2-}, $C_2O_4^{2-}$, BO_3^{3-}, tartrate and citrate do not interfere.

For the gravimetric determination[27,28] cobalt is precipitated quantitatively with an ethanolic solution of the reagent in the pH range 3·0–6·0 in the presence of ammonium chloride or nitrate. The complex can be weighed as such, $Co(C_9H_9NO_4)_3$, after drying at 120–170° or as $CoSO_4$ after treatment with sulphuric acid. In amounts ten times that of the cobalt, Cd(II), Zn(II), Mn(II), Al(III) and Cr(III) do not interfere. Nickel can be tolerated in amounts equal to that of cobalt but CH_3COO^-, $C_2O_4^{2-}$, $C_4H_4O_6^{2-}$ and PO_4^{3-} interfere. In a mixture of palladium and cobalt, the latter can be estimated[29] in the filtrate after separation of palladium with this reagent.

Iron

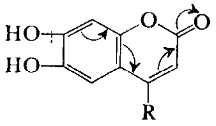
3-Acetyl-4-hydroxycoumarin has been used for the spectrophotometric determination of iron(II)[30] with which it forms an orange 3:1 ligand:metal complex soluble in aqueous ethanol. The complex has maximum absorption at 400 mμ, obeys Beer's law over the range 1·5–5·3 ppm of iron and is unaffected by acidity over the pH range 2·8–4·3. The tolerances for various ions in determination of 2 ppm of iron are: Cl^-, Br^-, I^-, SCN^-, Na and K 200 ppm each; Mg(II) 125 ppm; Pb(II) 115 ppm; Mn(II) 15 ppm; $C_2O_4^{2-}$ 10 ppm; Ni(II) 5·8 ppm; Be(II) 4·5 ppm. Even extremely small quantities of Cu(II), MoO_4^{2-}, WO_4^{2-} and citrate interfere.

Oximidobenzotetronic acid forms a deep blue, water-soluble complex with iron(II),[31] absorption maximum 625 mμ. A similar reaction occurs with iron(III) but with iron(II) the reaction is more sensitive and rapid. The iron(II) complex is stable over the pH range 2·5–10·0, and obeys Beer's law over the range 0·54–5·4 ppm of iron; its absorbance is unaffected by temperature between 10 and 50°. The reagent is fairly selective for iron, only cobalt, nickel, cerium, zirconium and some of the platinum metals giving serious interference. Oximidobenzotetronic acid has also been used[32] for gravimetric determination of iron(II), in the presence of tenfold amounts or more of Mn(II), Al(III), Cr(III), Ti(IV), Zr(IV), Th(IV), Ni(II), Zn(II), Mo(VI), Ca(II), Mg(II), CH_3COO^-, F^-, SCN^-, PO_4^{3-}, citrate, tartrate, W(VI), Cu(II), Bi(III) and Sn(II). The interference due to the last four ions was eliminated by using tartaric acid as masking agent. Cerium(III) and (IV), vanadium(V) and EDTA interfere. The final alcohol concentration was kept below 5%, the pH was varied from 0·8 to 9·0 and large amounts of ammonium chloride or nitrate were added.

The qualitative application of the colour reaction between iron and esculetin was reported by Casparis and Manella,[33] followed by more detailed investigations by others.[34] It has been shown that iron(III) forms two water-soluble complexes, an unstable green one at pH 0·5–4·5, and a comparatively stable red one at pH > 7·0. The latter is a 3:1 ligand:iron complex, shown by electrophoretic studies to be negatively charged. Iron can be estimated with this reagent in the presence of F^-, Cl^-, Br^-, I^- CH_3COO^-, SCN^-, $C_2O_4^{2-}$, $C_4H_4O_6^{2-}$, BO_3^{3-}, PO_4^{3-} and citrate though most cations interfere owing to their precipitation at high pH.

Molybdenum

In esculetin and its derivatives the 7-hydroxy group is very reactive owing to electromeric effects indicated in structure XIV. When a nucleophilic group such as methyl or phenyl is substituted in the 4-position, the dissociation of the 7-hydroxy group decreases and the ligand becomes less acidic. When complex formation between molybdenum and esculetin or its derivatives was studied[35] it was found that stability of the complex increases with basicity of the ligand. Molybdenum(VI) complexes formed with esculetin, 4-methylesculetin and 4-phenylesculetin are orange-red and show maximum absorption between 384 and 415 mμ. Between pH 5·5 and 6·0 the complex obeys Beer's law up to 4·8 ppm of molybdenum. Fe, Ti, Th, Ce, V, W, citrate and acetate ions interfere seriously. The complexes are 2:1 ligand:molybdenum.



(XIV)

Similarly, complex formation between molybdenum(VI) and daphnetin or its 4-methyl and 4-phenyl derivatives has been studied.[6] In each case the complex formed is orange-red, water-soluble and has $\lambda_{max} \sim 400$ mμ. The major species formed is 1:2 molybdenum:ligand but the presence of a lower complex (1:1) is also indicated. Ce, Fe, Ti, Th, V, Nb, W, U, Be, Mn, Zn, Cd, citrate, fluoride and oxalate interfere.

The 1:1 yellow complex[36] formed when 3-phenyldaphnetin reacts with molybdenum(VI) has λ_{max} 400–410 mμ in the pH range 1–7 and obeys Beer's law between 1·7 and 5·7 ppm of molybdenum. The interfering ions are the same as for daphnetin and its 4-substituted derivatives.

Niobium and tantalum

Niobium has been quantitatively precipitated and separated from tantalum and molybdenum with 4-phenyldaphnetin[37] at pH 5·0–8·5; the complex is ignited to Nb_2O_5 which is then weighed. From infrared studies it appears that the hydrogen atoms of the hydroxy groups are replaced by the metal ion. Tantalum is also precipitated quantitatively at pH 5·0–8·5 but the precipitate is insoluble in alcohol, in contrast to the alcohol-soluble niobium complex. This difference in solubility has been utilized for the separation of niobium and tantalum. Molybdenum(VI) forms an orange-red water-soluble complex with an alcoholic solution of 4-phenyldaphnetin. 7,8-Dihydroxy-4-methylcoumarin has also been used for quantitatively precipitating niobium and tantalum.[38]

Esculetin and its 4-methyl derivative form orange-red water-soluble complexes with niobium and these have been investigated for its spectrophotometric determination[39] at pH 6·5 and 400–405 mμ. The colour of the complexes remains unchanged for 72 hr and they obey Beer's law. The complexes have been assigned a 1:3 metal:ligand structure. For the esculetin complex log β is 10·43 and for the 4-methyl derivative it is 12·07. Be(II), Fe(II), Fe(III), Cu(II), Co(II), Pb(II), V(V), Mo(VI), Zr(IV), Ce(III), Ce(IV), Ti(IV), Ta(V), W(VI), SCN^-, CH_3COO^-, PO_4^{3-} and citrate interfere.

Platinum metals

Oximidobenzotetronic acid has been recommended for the gravimetric determination of palladium.[40] An ethanolic solution of the reagent quantitatively precipitates Pd(II) as $Pd(C_9H_5NO_4)_2$ at pH 0–5·1. In 0·5*N* acid solution, Fe(III), Ni(II), Ru(III), Rh(III), Os(IV), Ir(IV), Pt(IV), Cr(III), Mo(VI), Se(VI), Te(VI), As(V), Sb(III), Bi(III), Ti(IV), Zr(IV), Pb(II), Al(III), Zn(II), Cd(II) Hg(II), Cu(II), Ag(I), Au(III), CH_3COO^-, F^-, $C_2O_4^{2-}$, $C_4H_4O_6^{2-}$, PO_4^{3-} and citrate do not interfere. Cobalt can be determined in the filtrate.

Spectrophotometric studies of the coloured complexes[41] formed by oximidobenzotetronic acid (OBTA) with ruthenium and rhodium have been carried out and the two metals simultaneously determined. Ru(III) forms a purple-violet complex (λ_{max} 520 mμ) which is stable in the pH range 1·1–11·4 and contains ruthenium and ligand in 1:3 molar ratio. Ion-exchange studies show the complex is uncharged. The complex obeys Beer's law from 0·45 to 20·25 ppm of ruthenium and its molar absorptivity is $7{\cdot}08 \times 10^3$. Rh(III) forms a yellow-brown complex (λ_{max} 385 mμ) at pH 2–8 but at higher pH(>11·5) the complex is reddish-brown with λ_{max} 475 mμ. From ion-exchange studies both complexes appear to be $[RhCl_2(C_9H_4NO_4)_2]$. The red complex obeys Beer's law from 0·7 to 15·7 ppm of rhodium and its molar absorptivity is $7{\cdot}06 \times 10^3$. Large amounts of NO_2^-, NO_3^-, Cl^-, CH_3COO^-, F^-, SO_4^{2-}, $C_2O_4^{2-}$, $C_4H_4O_6^{2-}$, BO_3^{3-}, PO_4^{3-} and citrate do not interfere but iron(II), cobalt(II) and other platinum metals do.

OBTA has been used for spectrophotometric determination of iridium.[42] Boiling chloroiridate(IV) with ethanolic OBTA solution at pH 10–12 yields an anionic wine-red complex with absorption maximum at 476 mμ. The molar absorptivity is $9{\cdot}05 \times 10^3$ and log β is 12·5 ± 0·2 (at 30° in 30% ethanol). Ru(III), Fe(II), Co(II), Pd(II), Rh(III) and Pt(IV) interfere but Os(IV), Ni(II), Pb(II), NO_3^-, Cl^-, ClO_4^- do not.

Complexes of OBTA with Os(IV) and Pt(IV) have been studied spectrophotometrically.[43] Ethanolic OBTA solution forms an anionic brown-red 3:1 complex (λ_{max} 520–540 mμ) with chloro-osmate(IV), stable over the pH range 1·1–5·0. With chloroplatinate(IV) two complexes have been characterized, one being yellow (λ_{max} 425 mμ) and stable at pH 1·6–4·0, and the other red (λ_{max} 480 mμ) and stable only at pH > 10·2; both complexes are 2:1 and anionic. A method for the separation of Ru(III) from other platinum metals by use of Amberlite IRA–410 resin has been suggested, since the Ru–OBTA complex is neutral. The formation constants (log β) for the Os(IV) and Pt(IV) complexes are 15·6 and 11·6 respectively.

Thorium

Thorium has been estimated gravimetrically at pH 2–4 with 3-acetyl-4-hydroxycoumarin.[44] Cerium(III) and lanthanum do not interfere. The thorium complex is very soluble in alcohol whereas the uranium(VI) complex is insoluble and this can be used to estimate thorium in presence of uranium. 7,8-Dihydroxy-4-methylcoumarin has also been recommended for determining thorium.[45]

Titanium

Many hydroxycoumarins have been used for gravimetric and spectrophotometric determination of titanium. The complexation of titanium with 3-acetyl-4-hydroxycoumarin in ethanolic solution takes place at pH 7·0–9·0.[46] The yellow precipitate is ignited to TiO_2. Patrovský[47] recommended 4-methyl-7,8-dihydroxycoumarin for the quantitative precipitation of titanium. A method[48] for the separation and estimation of titanium from iron(II) solutions with 4-phenyl-7,8-dihydroxycoumarin at pH 2·0–6·5 has been described. Even traces of tartrate, citrate, zirconium and EDTA interfere but large amounts of sulphate, acetate and oxalate can be tolerated. Titanium forms an insoluble complex with 4-phenylesculetin at pH 1·8–3·7 whereas iron(II) does not.[49] Tartrate, citrate, zirconium and EDTA interfere. The composition of the complex has been found by applying the method of continuous variations to the precipitated species, and is 1:1. No band is observed at 3500 cm^{-1} in the infrared spectrum of the complex indicating the absence of hydroxy groups, whereas there is such a band in the infrared spectrum of the free ligand. Evidently the hydrogen atoms of both hydroxy groups in the ligand are liberated in complex formation.

o-Dihydroxycoumarins and their derivatives have been used for spectrophotometric determination of titanium. All the chelates formed are 1:3 (metal:ligand). Esculetin and its 4-methyl derivative[50] form orange-red, water-soluble titanium complexes at pH 5·5. Daphnetin[51] has been used for estimating up to 3·0 ppm of titanium at pH 4·0–4·5, the tolerance limits (in ppm) for common anions being BO_3^{3-} (200), citrate (10), F^- (50), SO_4^{2-} (200), PO_4^{3-} (200) and $C_2O_4^{2-}$ (120) in determination of 0·5 ppm of titanium. 3-Benzyl-4,5-dihydroxycoumarin[52] has been used to determine titanium at pH 1·8–2·5. The system obeys Beer's law at 380 mμ up to 6·2 ppm of metal ion. The orange complex contains titanium and ligand in the ratio 1:3.

Uranium

Uranium has been separated from thorium and determined even in the presence of ten times its amount of Ce(III) and La(III) by use of 3-acetyl-4-hydroxycoumarin as precipitating agent.[44] The uranium complex is insoluble in aqueous ethanol but the thorium complex is soluble. The uranyl complex is soluble, however, in 95% ethanol and has been found to be 1:1 and to obey Beer's law at 380 mμ over the range 0–57 ppm of uranium.[53]

In view of Sommer's conclusion[54] that compounds containing *ortho* and *peri* dihydroxy groups are chromogenic for uranium, 3-phenyldaphnetin[55] and 3-benzyl-4,5-dihydroxy coumarin[56] were studied. 3-Phenyldaphnetin in ethanolic solution forms a water-soluble 1:1 orange-yellow complex with uranyl ions between pH 5·4 and 6·0. The complex obeys Beer's law up to 9 ppm of uranium; log β is 4·0 $\pm$ 0·2 at 30–32° in 30% alcoholic solution. Tolerance limits (ppm) for common anions are: BO_3^{3-} (30), citrate (10), F^- (20), $C_2O_4^{2-}$ (20), PO_4^{3-} (20), SO_4^{2-} (200). Th(IV), Fe(III), Co(II), Ni(II), Ti(IV), Ce(IV), Mo(VI) *etc.* interfere because of their tendency to complexation with *o*-dihydroxy ligands. Similarly, 3-benzyl-4,5-dihydroxycoumarin reacts with uranium at pH 4·0, forming an orange 1:1 complex soluble in 40% alcohol.

The complex obeys Beer's law up to 30 ppm of uranium; log β is 5·0 ± 0·2. Interferences are similar to those for 3-phenyl daphnetin.

Zirconium

The complex formed between zirconium and 3-acetyl-4-hydroxycoumarin[46] has been used for gravimetric determination of zirconium. The complex obtained at pH 3·5–7·0 is finally ignited to ZrO_2 and weighed.

Zirconium forms an insoluble 1:1 complex with 4-phenylesculetin[49] in the pH range 2·0–3·0 whereas iron(II) does not. This fact has been utilized to separate these two ions. That complexation takes place through the hydroxy groups is proved from infrared studies. Tartrate, citrate and EDTA interfere but acetate, oxalate and sulphate do not. 4-Phenyldaphnetin[57] has also been used for gravimetric determination of zirconium at pH 1·8–7·5. The light yellow, alcohol-soluble complex is contaminated with excess of reagent, which cannot be readily washed out, so it is ignited to the oxide and weighed. Interferences are similar to those for the esculetin method.

CONCLUSION

It is evident that hydroxycoumarins are potentially useful analytical reagents. They give quite sensitive reactions and can be made selective by appropriate variation in pH or alcohol concentration and the use of suitable masking agents. They can be used with advantages in the detection and determination of many metals by spectrophotometric and gravimetric techniques. Certain analytically important separations and subsequent estimations have been performed with their aid.

Acknowledgement—The authors are grateful to Prof. B. D. Jain for constant encouragement and to the University Grants Commission (India) for the scheme "Analytical Study of Chelates" under which the present review has been written.

Zusammenfassung—Es wird eine Übersicht über die analytischen Möglichkeiten und die physikalish-chemischen Eigenschaften von Hydroxycumarinen gegeben.

Résumé—On présente une revue sur les possibilités analytiques et les propriétés physico-chimiques d'hydroxycoumarines.

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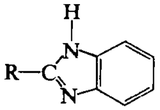
SHORT COMMUNICATIONS

New chromogens of the ferroin type—III
Some 2-substituted benzimidazole derivatives

(*Received* 4 *March* 1968. *Accepted* 13 *April* 1968)

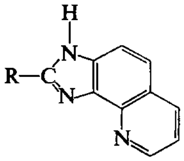
THE PREPARATION of 23 new ferroin-type chromogens was recently reported by Case.[1] The compounds are derivatives of benzimidazole or imidazole, with pyridyl, quinolyl, 2,2′-bipyridyl or 1,10-phenanthrolyl groups substituted for hydrogen at the 2-position of the imidazole ring. All contain one or more possible ferroin-type groupings $—\mathrm{N}{=}\overset{|}{\mathrm{C}}—\overset{|}{\mathrm{C}}{=}\mathrm{N}—$. The results of a spectrophotometric study of their reactions with iron(II) and copper(I), carried out with samples provided by Dr. Case, are reported here. The compounds will be referred to by combined roman numeral (derivative type) and letter (substituent) designation; structures and identities are given below.

I. 2-Substituted benzimidazoles



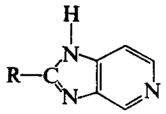
	R
IA	4-Methyl-2-pyridyl
IB	4-Phenyl-2-pyridyl
IC	2-Quinolyl
ID	2,2′-Bipyridin-6-yl
IE	2-Phenanthrolyl

II. 2-Substituted 2*H*-imidazo[4,5-*h*]quinolines



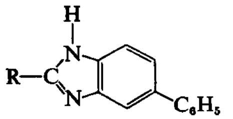
	R
IIA	2-Pyridyl
IIB	4-Methyl-2-pyridyl
IIC	4-Ethyl-2-pyridyl
IID	4-Phenyl-2-pyridyl
IIE	2,2′-Bipyridin-6-yl
IIF	2-Phenanthrolyl

III. 2-Substituted 1*H*-imidazo[4,5-*c*]pyridines



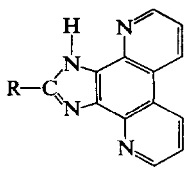
	R
IIIA	2-Pyridyl
IIIB	4-Methyl-2-pyridyl
IIIC	4-Phenyl-2-pyridyl
IIID	2,2′-Bipyridin-6-yl

IV. 2-Substituted 5(6)-phenylbenzimidazoles



	R
IVA	2-Pyridyl
IVB	4-Methyl-2-pyridyl
IVC	4-Phenyl-2-pyridyl
IVD	2,2′-Bipyridin-6-yl

V. 2-Substituted 1*H*-imidazo[4,5-*f*][4,7]phenanthrolines



	R
VA	2-Pyridyl
VB	4-Methyl-2-pyridyl
VC	4-Phenyl-2-pyridyl
VD	2,2′-Bipyridin-6-yl

EXPERIMENTAL

The syntheses and analyses of the new compounds have been reported by F. H. Case,[1] who furnished the samples used in the present study.

A description of the various standard solutions, pH buffers, and reagents appears in an earlier publication of this series.[2] The procedures used for studying complex formation and for determining absorption characteristics have also been described previously.[2] All of the solutions prepared for spectrophotometric examination were diluted to volume with ethanol in order to attain complete dissolution of the complexes. Mole-ratio and continuous variations studies were performed by conventional procedures.[3,4]

TABLE I.—PROPERTIES OF THE METAL CHELATES

Metal ion	Chromogen	Chelate colour	pH Range for max. colour	λ, mμ	ε
Fe^{2+}	IA	red	4–6	502	2200
		purple	11–12	525	2200
	IB	red	4–6	520	4100
		purple	11–12	540	4200
	IC	yellow	4–6	416*	800
		yellow	11–12	450*	900
	ID	red	4–6	558	8400
		blue	8–12	608	6600
	IE	magenta	4–6	583	9600
		blue	8–12	603	11900
	IIA	yellow	4–9	450*	600
		orange	11–12	460*	1000
	IIB	yellow	4–9	488*	500
		orange	11–14	490*	1000
	IIC	yellow	4–6	438*	300
		orange	8–11	450*	600
	IID	orange	4–6	462	600
		red ppt.	8–12	—	—
	IIE	red	4–6	554	7300
		blue	8–12	605	5700
	IIF	purple	4–6	565	6200
		blue	8–12	597	10700
	IIIA	magneta	4–6	533	2300
		purple	8–12	548	3200
	IIIB	magenta	4–6	542	1900
		purple	8–12	548	2800
	IIIC	red	4–6	569	5000
		purple	11–12	588	9500
	IIID	magenta	4–6	566	9600
		purple	8–12	593	7400
	IVA	red	4–6	512	2300
		purple	8–12	550	2600
	IVB	red	4–6	505	2400
		purple	8–12	520	2500
	IVC	magenta	4–6	547	5400
		blue	8–12	606	7100
	IVD	red	4–6	570	7000
		blue	8–12	611	5900
	VA	yellow	5–11	470*	700
	VB	yellow	5–11	470*	600
	VC	orange	7–11	475*	1000
	VD	magenta	5–7	570	7000
		blue	8–12	611	5900
Cu^{+}	IC	orange	4–7	483	3600
	ID	yellow	10–14	425*	16000
	IIE	yellow	10–14	425*	15800
	IIID	yellow	12–14	415*	14400
	IVD	yellow	10–14	410*	13000

* Shoulder; absorption band of complex overlaps that of free ligand.

RESULTS

The chromogenic properties of the benzimidazole derivatives with respect to iron(II) chelation are inferior to those of 1,10-phenanthroline and other popularly used ferroin-type chromogens. Compound IE forms the most intensely coloured iron(II) chelate of the group studied; however, its maximum molar absorptivity (Table I) is only slightly greater than that of the iron(II) complex of 1,10-phenanthroline ($\varepsilon = 11100$ at 510 mμ), which is reasonable considering the close relationship between the two.

Spectral characteristics of the various iron(II) chelates are appreciably pH-dependent. In general, wavelengths of maximum absorbance increase with increasing pH over the pH range from approximately 6 to 10. The bathochromic shifts probably arise as a consequence of the increasing extent of ionization of the weakly acidic imino hydrogen groups with increasing pH. In this connection, Harkins and Freiser[5] found that metal–ion co-ordination enhances the acidity of 2-(2-pyridyl)-benzimidazole. Absorptivities also generally show enhancement with increasing pH. An interesting exception is noted in the case of the 2,2′-bipyridin-6-yl derivatives (ID, IIE, IIID, IVD, and VD) which undergo a decrease in absorbance as solutions of their iron(II) chelates are made strongly alkaline.

All of the iron(II) complexes except that of IC can be extracted quantitatively into isoamyl alcohol. Solubilities are low in water but adequate in ethanol–water mixtures.

Ligand-to-iron(II) ratios for some representative complexes are given in Table II. These experimental values agree with the ratios expected from structural considerations. The tris–chelates are much less stable than the bis-chelates as evidenced by considerable curvature in the mole-ratio plots. This indicates that the imidazole ring is less favourable for iron chelation than either a pyridyl or phenanthroline moiety when incorporated into a ferroin-type grouping. Stability as well as colour-sensitivity suffers. Similar results were found by Walter and Freiser[6] for the iron(II) chelates of 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)-imidazoline.

TABLE II.—IDENTITIES AND RELATIVE STABILITIES OF REPRESENTATIVE IRON(II) COMPLEXES AS DETERMINED BY CONTINUOUS VARIATIONS AND MOLE-RATIO METHODS

Chromogen	Ligand-to-metal ratio	Relative stability*
IA	3:1	low
ID	2:1	high
IE	2:1	high
IIA	2:1	high
IIIA	3:1	low
IVA	3:1	low
VA	2:1	high

* Estimated on basis of curvature in the mole-ratio plots.

Only five of the new compounds give any appreciable colour with copper(I). The complexes are extractable into isoamyl alcohol. Other properties are listed in Table I. Spectral characteristics of the copper(I) complexes do not show the same pH-dependence as the iron(II) complexes. The absorption bands of the copper(I) complexes are either relatively weak or they overlap bands of the uncomplexed compounds. None of the new compounds are considered promising as copper chromogens.

Acknowledgement—This investigation was supported by a grant from the G. Frederick Smith Chemical Company. Samples of the compounds were furnished by Dr. Francis H. Case. K. R. Kluge received support as a National Science Foundation Undergraduate Research Participant, (Summer 1967).

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Summary—A spectrophotometric study has been made of the iron(II) and copper(I) chelates of 23 new compounds that contain the ferroin functional grouping. Although none of the compounds proved to be superior to chromogenic reagents currently in use, the results are of interest from the point of view of designing new chromogens for iron and copper.

Zusammenfassung—23 neue Verbindungen, die die funktionelle Gruppierung des Ferroins enthalten, wurden als Eisen(II)- und Kupfer(I)-chelate spektrophotometrisch untersucht. Obwohl sich keine Verbindung den zur Zeit üblichen farbbilden Reagentien überlegen erwies, sind die Ergebnisse im Hinblick auf die Suche nach neuen Farbbildern für Eisen und Kupfer von Interesse.

Résumé—On a effectué une étude spectrophotométrique des chélates du fer (II) et du cuivre (I) avec 23 nouveaux composés qui contiennent le groupement fonctionnel ferroïne. Bien qu'aucun de ces composés ne se soit révélé supérieur aux réactifs chromogènes couramment en usage, les résultats sont intéressants du point de vue de la conception de nouveaux chromogènes pour le fer et le cuivre.

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Differential spectrophotometry of nickel as its pyridine-2,6-dicarboxylic acid complex

(*Received* 22 *December* 1967. *Accepted* 1 *March* 1968)

NICKEL(II) forms a 1:2 complex with pyridine-2,6-dicarboxylic acid (PDC), that appears to have suitable properties for the differential spectrophotometric determination of nickel. The complex is formed immediately the two compounds are mixed. The absorption spectrum of the compound, given in Fig. 1, appears to be very reproducible, independent of the excess of complexing agent or of changes in pH in the range 2·5–10·5. The colour is stable for months and the absorption spectrum is the same in chloride, fluoride, sulphate, acetate and citrate media. The molar absorptivity is about 33 at 1025 mμ, the maximum in the absorption curve; this is much larger than the value for nickel

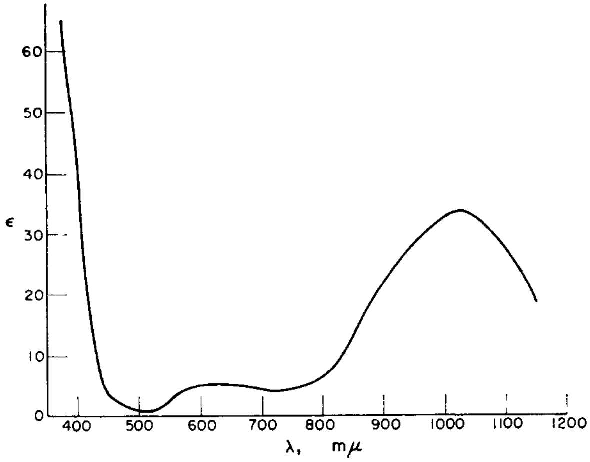

FIG. 1.—Absorption spectrum of the complex of Ni(II) with pyridine-2,6-dicarboxylic acid.

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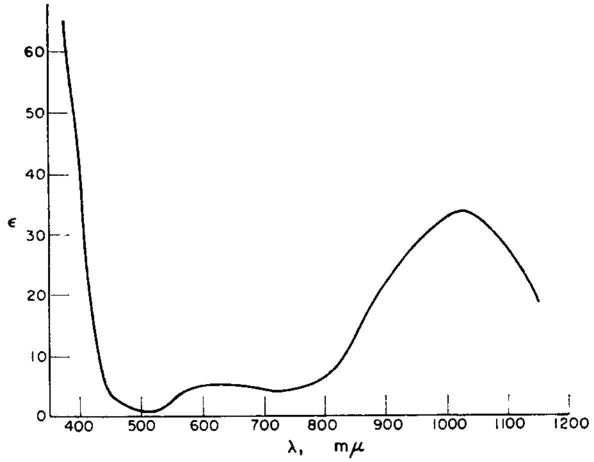

FIG. 1.—Absorption spectrum of the complex of Ni(II) with pyridine-2,6-dicarboxylic acid.

perchlorate (about 1·5 at 720 mμ) which has been used for the precision spectrophotometry of nickel. The differential spectrophotometric determination of nickel can therefore be extended to more dilute solutions or to samples with lower nickel contents, by use of this complex. There are also fewer interfering elements than in the perchlorate method, mainly because the nickel complex absorbs in a different wavelength region from the PDC complexes of the interfering elements.

EXPERIMENTAL

All chemicals used were of analytical grade. PDC was used as a solution of its sodium salt. Nickel sulphate solutions were standardized by photometric titration with EDTA, Murexide being used as indicator. A weight burette was used, and the error in the nickel determination was $<0·1\%$ at the 95% confidence limits. Portions of the nickel solution for the calibration curves were taken by weight. The only volumetric glassware used was the 100-ml volumetric flasks (calibrated before use).

A Zeiss PMQ II spectrophotometer was used, with the temperature kept constant at 20 ± 2°; the slit-width was 0·20 mm; the sensitivity varied from set to set depending on the absorbance of the blank. The wavelength used was 1025 mμ; the tungsten lamp and a lead sulphide detector cell were used. Cells were carefully cleaned and corrections were made for differences in path-length. The nickel complex was obtained at pH 5–6; this pH value is automatically reached when a solution of the sodium salt of PDC is added in excess to a slightly acid sample. The excess should refer to all ions forming PDC complexes.

RESULTS AND DISCUSSION

Three calibration curves were made, covering the absorbance ranges 0–1, 1–2 and 2–3, Ni-PDC solutions with absorbances 0, 1 and 2 respectively being used as blanks. All three appeared to be straight lines with the same slope, demonstrating that Beer's law was obeyed over a large concentration range. A series of determinations of nickel was made by the transmittance ratio method,[2] in the concentration range 0·03M, corresponding to an absorbance of 1. All determinations were carried out by using a reference solution with a slightly lower nickel concentration, prepared by weighing an appropriate amount of the nickel sulphate standard solution into a 100 ml flask, adding PDC reagent in excess and filling the flask to the mark. The accuracy of the method was tested as well as the effect of the presence of other ions. The nickel content of the solutions was calculated by means of the equation

$$c = \frac{A}{0·573} + b$$

where c is the nickel content of the unknown in mg/ml, and A the absorbance of the unknown solution, measured with a nickel-PDC solution containing b mg of nickel per ml as reference solution. The constant 0·573 ml/mg was determined by careful calibration.

It appeared that no interference occurred when nitrate, nitrite, perchlorate, citrate, acetate, Cr(VI), Mn(II) V(V), Zn, Mg, Al, alkaline earth and alkali metals were present up to a level of 5 mg/ml. Cobalt and copper interfere because of the absorption of their PDC complexes at 1025 mμ but 1% of cobalt and 0·1% of copper (with respect to nickel present) can be tolerated. Determinations in the presence of Cr(III) are possible, but the accuracy is not as good as in its absence. This is caused by the necessity to heat the solution in order to establish the Cr(III)-PDC complex in reasonable time. Iron(III) seriously interferes when present in an amount of 2 mg/ml. Up to 0·2 mg/ml can be tolerated but the precision is poorer than in the absence of iron. As the interference is probably due to the presence of small amounts of Fe(II), a drop of hydrogen peroxide improves the accuracy, but the peroxide may interfere when other metals are present. Some results for nickel in the presence of interfering elements are given in Table I. The method was used to determine the nickel content of

TABLE I.—DETERMINATION OF NICKEL IN THE PRESENCE OF INTERFERING IONS

Ni content, *mg/ml*		Other elements, *mg/ml*	Error, %
taken	found		
1·782	1·798	0·2 Fe(III)	+1
1·766	1·790	0·2 Fe(III)	+1·5
1·802	1·811	0·2 Fe(III); 1 drop H_2O_2	+0·5
1·744	1·755	0·2 Fe(III); 1 drop H_2O_2	+0·6
1·785	1·784	0·02 Co(II)	−0·1
1·790	1·787	0·002 Cu(II)	−0·2
1·760	1·755	2 Cr(III)	−0·3
1·780	1·766	2 Cr(III)	−0·8
1·778	1·775	2 Cr(III)	−0·2
1·783	1·774	1 Cr(III)	−0·5

high purity nickel oxide and nickel wire. The results for the oxide were NiO, 100·7%; 100·8%; 100·7%; 100·6%: for the nickel wire they were Ni, 99·7%; 99·6%; 99·8%. These and many other results gave a relative standard deviation of 0·1% for the method in this concentration region, which demonstrates that the method is very useful for the precision spectrophotometric determination of nickel.

Acknowledgement—The authors wish to thank Mrs. I. G. Asscher-Wolanska, who carried out the larger part of the experimental work.

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Summary—The determination of nickel with pyridine-2,6-dicarboxylic acid by means of differential spectrophotometry at 1025 mμ is described. At the Ni concentration level of 2 mg/ml the relative standard deviation is 0·1%. Only a few elements interfere.

Zusammenfassung—Die Bestimmung von Nickel mit Pyridin-2,6-dicarbonsäure durch Differenz-Spektrophotometrie bei 1025 nm wird beschrieben. Bei Nickelkonzentrationen um 2 mg/ml ist die relative Standardabweichung 0,1%. Nur wenige Elemente stören.

Résumé—On décrit le dosage du nickel par l'acide pyridine 2,6-dicarboxylique au moyen d'une spectrophotométrie différentielle à 1025 mμ. Au niveau de concentration en Ni de 2 mg/ml l'écart type relatif est de 0,1%. Seuls quelques éléments gênent.

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Homogeneous nucleation of bis(1,2-cyclohexanedionedioximato)palladium(II)

(*Received* 15 *January* 1968. *Accepted* 19 *April* 1968)

The droplet technique, first described by Vonnegut,[1] has been used with considerable success in the study of homogeneous nucleation of a large variety of substances.[2-6] This method involves the subdivision of the sample under study into a very large number of non-communicating droplets. The foreign particles capable of acting as nucleation catalysts in the original sample are presumably sequestered by incorporation into a small fraction of the droplets, which will undoubtedly exhibit heterogeneous nucleation. However, most of the droplets should remain catalyst free, so homogeneous nucleation is expected to occur in them.

In most droplet experiments the supersaturation required to induce nucleation has been attained by gradually lowering the temperature of the system. In 1966 Hileman,[7] and Thompson and Gordon,[8] while studying the nucleation of metal chelates, utilized the technique of precipitation from homogeneous solution as the means of achieving supersaturation in the droplets. This paper describes recent studies on the nucleation of bis(1,2-cyclohexanedionedioximato)palladium(II) in which supersaturation was obtained by reaction between 1,2-cyclohexanedione and hydroxylamine in the presence of palladium ions.

EXPERIMENTAL

Solutions containing palladium(II), hydrochloric acid, hydroxylamine hydrochloride and 1,2-cyclohexanedione were prepared by mixing, in the order given, various amounts of their stock solutions. Immediately after the last reagent was added the solutions were dispersed in mineral oil. The dispersions, which consisted mostly of droplets of about 20 μ in diameter, were then examined with a polarizing microscope and the crystallization occurring in the droplets was recorded photographically.

RESULTS AND DISCUSSION

From the photographs the nucleation rate was obtained, and plotted as a function of time. The results of the experiments are demonstrated in Fig. 1.

high purity nickel oxide and nickel wire. The results for the oxide were NiO, 100·7%; 100·8%; 100·7%; 100·6%: for the nickel wire they were Ni, 99·7%; 99·6%; 99·8%. These and many other results gave a relative standard deviation of 0·1% for the method in this concentration region, which demonstrates that the method is very useful for the precision spectrophotometric determination of nickel.

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Homogeneous nucleation of bis(1,2-cyclohexanedionedioximato)palladium(II)

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THE droplet technique, first described by Vonnegut,[1] has been used with considerable success in the study of homogeneous nucleation of a large variety of substances.[2–6] This method involves the subdivision of the sample under study into a very large number of non-communicating droplets. The foreign particles capable of acting as nucleation catalysts in the original sample are presumably sequestered by incorporation into a small fraction of the droplets, which will undoubtedly exhibit heterogeneous nucleation. However, most of the droplets should remain catalyst free, so homogeneous nucleation is expected to occur in them.

In most droplet experiments the supersaturation required to induce nucleation has been attained by gradually lowering the temperature of the system. In 1966 Hileman,[7] and Thompson and Gordon,[8] while studying the nucleation of metal chelates, utilized the technique of precipitation from homogeneous solution as the means of achieving supersaturation in the droplets. This paper describes recent studies on the nucleation of bis(1,2-cyclohexanedionedioximato)palladium(II) in which supersaturation was obtained by reaction between 1,2-cyclohexanedione and hydroxylamine in the presence of palladium ions.

EXPERIMENTAL

Solutions containing palladium(II), hydrochloric acid, hydroxylamine hydrochloride and 1,2-cyclohexanedione were prepared by mixing, in the order given, various amounts of their stock solutions. Immediately after the last reagent was added the solutions were dispersed in mineral oil. The dispersions, which consisted mostly of droplets of about 20 μ in diameter, were then examined with a polarizing microscope and the crystallization occurring in the droplets was recorded photographically.

RESULTS AND DISCUSSION

From the photographs the nucleation rate was obtained, and plotted as a function of time. The results of the experiments are demonstrated in Fig. 1.

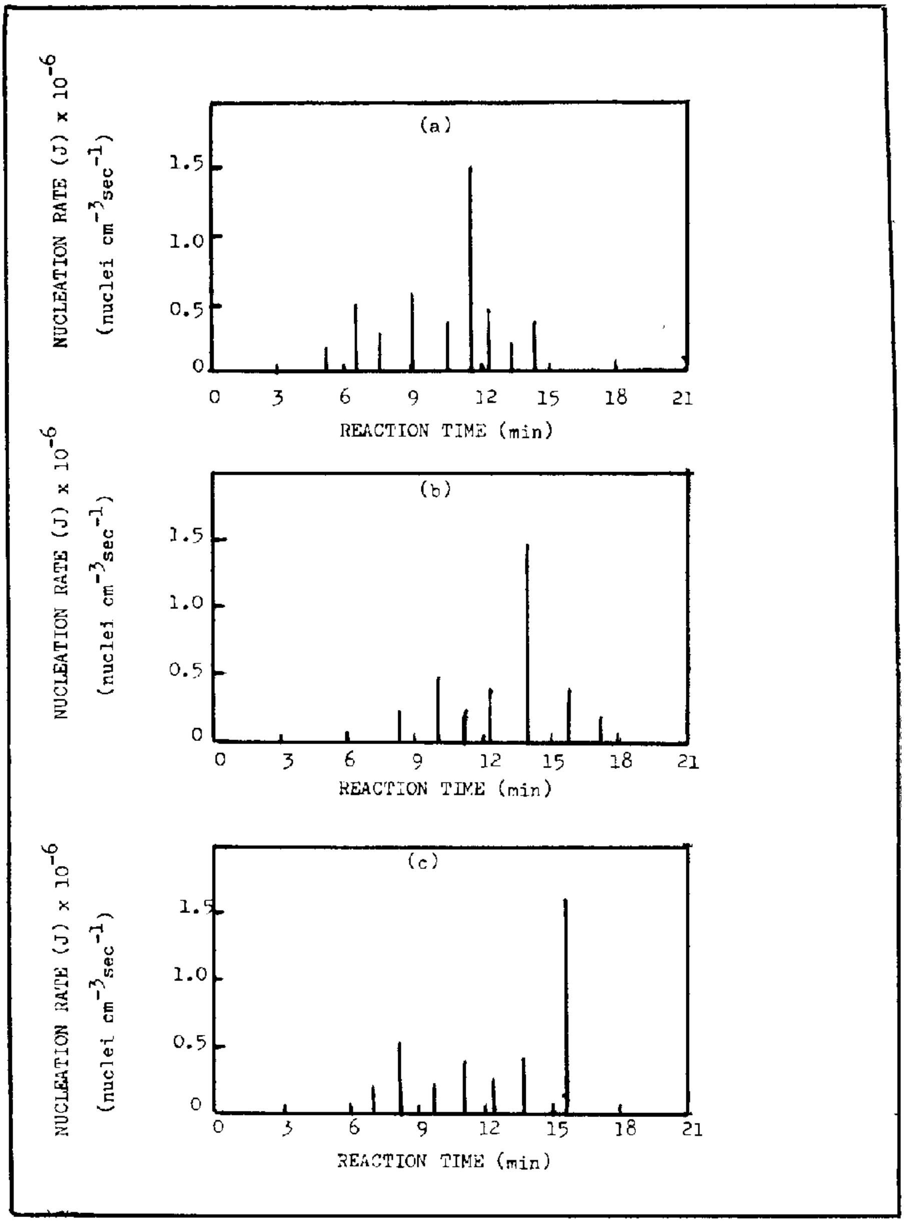

Fig. 1.—Nucleation rate *vs.* reaction time for the palladium chelate.

	Reaction conditions, [HCl], *M*	[Pd(II)], *M*	[NH$_2$OH.HCl], *M*	[C$_6$H$_8$O$_2$], *M*
(*a*)	1·0	0·1	0·7	0·2
(*b*)	1·0	0·1	0·7	0·1
(*c*)	1·0	0·1	0·3	0·1

One point of very high nucleation rate was observed for each of the three sets of concentrations employed. The position of this point was reproducible and occurred 11·5, 14·0 and 15·5 min after mixing the reagents (see Fig. 1). Filtering the reagent solutions through membrane filters of various pore sizes before the preparation of the dispersion did not alter the results.

Gravimetric analysis[9] showed that when the reagents were mixed in the proportions corresponding to the set of concentrations listed under Fig. 1*a*, the precipitate was produced at a constant rate of 0·38 $mg.ml^{-1}.min^{-1}$. At this rate the concentration of monomers in the droplets should rise to about $10^{-2}M$ after 11·5 min of reaction. Spectrophotometric analysis showed that the palladium content of a saturated solution of the chelate in $1M$ hydrochloric acid was about $10^{-5}M$. This implies that the supersaturation existing in the droplets at the point of maximum nucleation rate was 10^3.

According to the Volmer[10] theory of homogeneous nucleation the rate of nucleation is expressed as

$$\log_{10} J = \log_{10} A - \frac{16\pi\sigma^3 v^2}{3(2{\cdot}303kT)^3(\log_{10} S)^2}$$

where J is the nucleation rate, A is the kinetic constant, σ is the interfacial free energy, v is the molecular volume of the solid solute, k is the Boltzmann constant, T is the absolute temperature at which the experiment was carried out, and S is the supersaturation ratio. J was found to be of the order of 10^6 $nuclei.cm^{-3}.sec^{-1}$. Assuming $A = 10^{30}$ $cm^{-3}.sec^{-1}$, σ was found to be 47 $erg.cm^{-2}$ for the chelate.

Several expressions have been derived which relate the supersaturation of a crystalline solid to the interfacial free energy and the particle size.[11] One such expression is the Gibbs–Thomson equation which was originally derived for vapours but has also been found applicable to small particles in solution. We shall use it in the form $r^* = 2\sigma v/2{\cdot}303kT \log_{10} S$, where r^* is the size of the critical radius and the other symbols have the same meaning as before. The calculated value of r^* for the palladium compound was about 11 Å.

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Summary—Precipitation from homogeneous solution has been applied to the drop technique for the study of the homogeneous nucleation of bis(1,2-cyclohexanedionedioximato)palladium(II). It was found that under the experimental conditions employed the interfacial energy of the chelate was 47 $ergs.cm^{-2}$ and the critical radius size 11 Å.

Zusammenfassung—Auf die Tropfenmethode zur Untersuchung der homogenen Keimbildung von Bis(1,2-cyclohexandiondioximato)-palladium(II) wurde die Fällung aus homogener Losung angewandt. Unter den Versuchsbedingungen war die Grenzflächenenergie des Chelats 47 erg cm^{-2} und der kritische Radius 11 Å.

Résumé—On a appliqué la précipitation en solution homogène à la technique à la goutte pour l'étude de l'amorçage homogène du bis(1,2-cyclohexanedionedioximato)palladium(II). On a trouvé que, dans les conditions expérimentales employées, l'énergie interfaciale du chélate est de 47 ergs/cm^{-2} et la dimension du rayon critique 11 Å.

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LETTER TO THE EDITOR

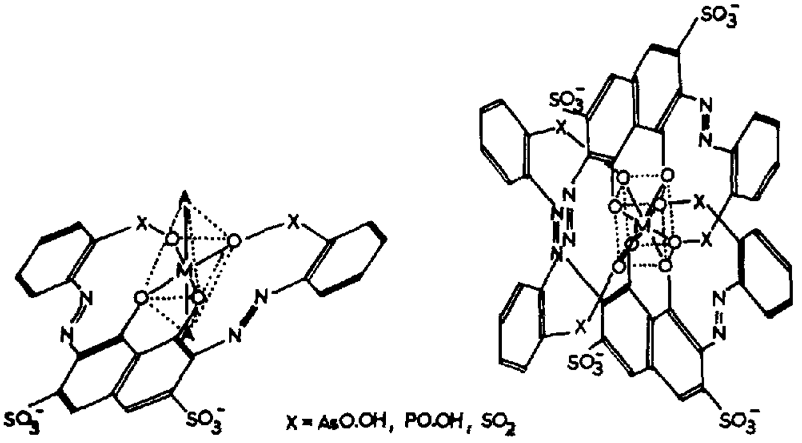
Structure of metal chelates of arsenazo III, phosphonazo III and sulphonazo III

SIR,

Arsenazo III,[1] 3,6-di(*o*-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid, phosphonazo III,[2] 3,6-di(*o*-phosphonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid, and sulphonazo III,[3] 3,6-di(*o*-sulphophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid, form metal chelates with molar ratio between metal and ligand 1:1 or 1:2. Detailed investigation of these metal chelates by the method of proportional absorbances[4] has shown that only mononuclear complex species are formed. The total symmetry of the reagents and the equivalent participation of both arsono, phosphono or sulpho groups in complex formation has been found from preparative and photometric studies.[5] Recent polarographic investigation[6] has also shown the absence of the free arsono group in the uranium(VI)-arsenazo III complexes. Unfortunately the structure proposed for these complexes in that paper[6] is not probable on stereochemical grounds. Other structures[1-8] are based on assumption of the presence of a free arsono, phosphono or sulpho (attached to benzene ring) group in the metal complex, which is not correct. Study of the composition of the lanthanum–arsenazo III complex in the pH range 1–3 gives the general formula LaH_4L; similarly the composition of the barium–sulphonazo III complex in the pH range 2–6 is BaH_2L.[7]

Previous variation in results[1,5] for complex composition may have been caused by insufficient purity of the reagents used and by quenching of absorbance caused by molecular association at higher concentrations of reagent (10^{-3}–$10^{-4}M$) at pH 4–7.

It may be assumed that arsenazo III, phosphonazo III and sulphonazo III act as quadridentate ligands and that their complexes are usually octahedral or cubic, see Fig. 1. Octahedral structure I corresponds to the composition metal:ligand 1:1 and co-ordination number 6 (or 4 for planar tetragonal complexes). Cubic structure II corresponds to the molar ratio 1:2 and co-ordination number 8. The square antiprism stereochemical configuration is less probable for 1:2 complexes since it seems to be connected with a distortion of the ligand planarity. Interatomic distances calculated from the geometry of structures I and II are compared with typical known metal–oxygen atom distances[8] in Table I. Good agreement of the calculated and known values may be seen.



I II

FIG. 1

TABLE I.—Comparison of calculated and known interatomic distances*

Optimum of O—M distance, Å					
Calculated		Known[8]			
arsenazo III	1·82	Be—O	1·331	Gd—O	1·79
phosphonazo III	2·05	Mg—O	1·749	Ho—O	1·78
sulphonazo III	2·15	Ca—O	1·822	Lu—O	1·77
		Sr—O	1·921	Zr—O	1·728
		Ba—O	1·940	Hf—O	1·71
		Ra—O	1·98	Th—O	1·89
		Y—O	1·790	U—O	1·92
		La—O	1·82		

* The distances given for *trans*-azobenzene and β-naphthol have been used for the calculation of arsenazo III, phoshonazo III, and sulphonazo III stereochemical models. Distances As—O, P—O, S—O, and O—M have been taken from the corresponding usual oxides of these elements.

Both structures I and II also give a good explanation for the extremely high stability and photometric sensitivity of metal chelates of these reagents.[1,5]

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ALBERT ARTHUR SMALES

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This issue of Talanta is published in honour of Dr. Albert Arthur Smales and, in particular, celebrates his first 21 years at the Research Establishment of the United Kingdom Atomic Energy Authority at Harwell, where he holds the post of Head of the Analytical Sciences Division.

In introducing this issue it is not my purpose to present a minutely detailed biography of the man we are honouring but instead I want to recall some of the highlights of his career so far, as seen by a personal friend of many years standing.

Albert Smales began his career in analysis in 1932 as a junior assistant in the analytical laboratories of the (then) Billingham Division of I.C.I. Ltd. where he came under the stern eye of the late Mr. H. N. Wilson, an experience for which he has always been grateful. Unlike the present time, opportunities for University education were few and Smales took an external London University B.Sc. degree in chemistry in 1941 by evening class study. This was to be followed by A.R.I.C. in 1944, F.R.I.C. in 1951 and D.Sc. in 1965. In the early years of the war he worked on analysis of metals, catalysts, organic chemicals and on various aspects of uranium analysis as the Tube Alloys project got under way in the I.C.I. laboratories. I was working at Widnes Laboratory (General Chemicals Division) at that time and my first acquaintance with Smales's work came with the receipt of a report on the analytical chemistry of 'T'—on the west coast we would refer to uranium as 'X' or 'D' and never really knew if this fooled anyone, especially when we talked of X_3O_8! In mid-September 1944 I found myself in Oak Ridge, Tennessee; two or three weeks later Albert Smales appeared, to be followed shortly afterwards by (the late) Harold Evans from the Winnington laboratories and until our families arrived early in 1945 we lived together under the paternal eye of Dr. (now Sir John) Baxter. Our task at Oak Ridge was to advise on analytical research. Evans, with his long experience at Winnington, found plenty to do in the Y-12 factory and Smales and I moved into a huge empty suite of laboratories up in the "Townsite" area. Soon afterwards, Dr. E. F. Orleman arrived to be Head of our Group: we were to enjoy a very happy collaboration with him. We acquired some two dozen staff: some were civilians who already had some experience of work in the area and some were recruited from the army. The main problems concerned the analysis, especially for uranium content, of the non-radioactive plant liquids and effluents arising from the work-up of U-235 being obtained by electromagnetic separation in the "race-tracks" at Y-12. We clearly needed rapid methods and turned to the use of instrumental methods, then only in their infancy. A Hilger Spekker was commandeered in England and flown out to us and we also acquired one of the new Beckman DU Spectrophotometers. Smales took to polarography with enthusiasm and had the luxury of a 10" chart recorder! He acquired a grating spectrograph for emission work, with Cyrus Feldman to operate it. The general atmosphere was one of cheerful improvization and a willingness and determination to get on with the job (despite the fact that more than a few of those around had no clear idea of what the purpose of that job might be until 5th August 1945!). Smales tried to explain cricket to his staff and began to study baseball, in which he maintains a strong interest even now.

With the capitulation of Japan we were free to return home and it is perhaps worth mentioning that soon afterwards we wrote together a report on American analytical instrumentation, not a world-shattering or widely-read document, but for both of us a precursor of the life to come. In 1946 there were moves to set up a British atomic energy organization, and in 1947, Smales became the Analytical Chemistry Group Leader at the infant Harwell.

Harwell was established by the Ministry of Supply and part of the early work of Smales's Group was to help with the organization and development of methods of analysis for the laboratories of the factories at Springfields, Windscale and Capenhurst which were to supply the basic materials for British atomic energy projects. The United Kingdom Atomic Energy Authority was formed in July 1954 to manage these projects, which meant that the atomic energy laboratories at Woolwich and Chatham became Smales's responsibility; these laboratories continued their independent existence until late 1966 by which time all their staff and functions had been transferred to Harwell.

The prime purpose of the analytical research work at Harwell was to service the new materials being produced for use in power generation. Fortunately, the measurement techniques of analysis are much the same whether one is working on some unmentionable analysis of plutonium or the composition of a meteorite so that we can, through the publications of Albert Smales and his staff, gain a fair insight into the achievements of the Group. Neutron-activation analysis, made into a highly sensitive trace element technique by the development of the atomic reactor, was being used in America in 1947. Smales was developing and making original contributions to the development of this technique very soon after reaching Harwell; we find his first review of it in the Chemical Society's Annual Reports for 1949 and a stream of papers and regular reviews of the subject subsequently appeared. Thus many of the analysts in England and elsewhere who have subsequently used activation analysis in their laboratories owe much to pioneering work at Harwell. Of course, much of the Harwell work has been concerned with the determination of traces of almost every element in the periodic table in a wide variety of matrices and important advances have been made in this field with emphasis being placed on rapid and, where possible, non-destructive methods. Thus radioactivation was followed by gamma-ray spectrometry, square-wave and pulse polarography, isotope dilution (especially in conjunction with mass spectrometry), work on emission spectroscopy (the determination of gases in metals being particularly noteworthy), and more recently, X-ray fluorescence, electron spin and nuclear magnetic resonance, spark source mass spectrography, controlled potential coulometry and the application of computers to analysis.

Smales has always been interested in geochemistry since he began work on uranium at Billingham, when together with the late Professor Arthur Holmes he published a number of papers on uranium, thorium and lead in rocks and minerals. In 1952 he published the first determination of uranium in geochemical materials by activation analysis and since then, in collaboration with his staff at Harwell and visiting University people, he has determined many elements in materials such as granitic and basic rocks, sea-water, deep-sea sediments, minerals, iron and stony meteorites *etc.*

The original work on meteorites was concerned with the problem of obtaining accurate trace element determinations in these materials, in order that reliable "cosmic abundance" figures for the elements could be made. This is a basic and essential feature of modern geochemistry and cosmochemistry, and neutron-activation and isotope-dilution methods have played a vital role in this work. However, the study of meteorites, in their own right, has now developed into an important branch of cosmochemistry, and work at Harwell is now not only concerned with obtaining reliable data for trace element distribution in the many types of meteorites, but in using this information to aid our understanding of the origin and evolution of these objects.

That this work is important and as such has obtained international recognition is shown by the fact that Smales is one of the chosen recipients for samples which the Americans hope to bring back to earth from the moon in the not too distant future.

It should be mentioned that in recognition of his work at Harwell he was made an Officer of the Order of the British Empire in 1960.

Albert Smales has been in the forefront of the discussion about the place and status of "analytical chemistry" in the world today. Such have been the developments in instrumentation and technique embracing disciplines other than chemistry that he has argued that we should now talk of the "analytical sciences" and to convince us of his sincerity in this, when his former Analytical Chemistry Branch became a Division in its own right, it was named the Analytical Sciences Division.

His achievements at Harwell are fully documented in the open literature and in consequence available to all for study but what may be less evident is his generosity in giving time to extramural activities and this article would not be complete without some mention of these.

As his authority in the world of atomic energy has increased, so has the demand for his services as a lecturer in many parts of the world. But he has also served analytical chemistry in his activities with the various chemical societies and other science-based organisations. He is closely associated with numerous University Departments of Geology and the Mineralogical Department of the British Museum of Natural History, and he is well known in the International Association of Geochemistry and Cosmochemistry, in which he is now playing a prominent part on the Committee dealing with the analysis of standard geochemical samples. He was a founder-Committee member of what is now the Thames Valley Section of the Royal Institute of Chemistry, and has taken considerable interest in the work of the Analytical Chemistry Division of I.U.P.A.C., but perhaps his largest contribution has been to the work of the Society for Analytical Chemistry. He began to take a practical interest in this Society's work shortly after moving South. Inevitably his interest was first centred on the Physical Methods Group which had been formed only a few years previously. He was a member of the Group Committee for several years and became its Chairman for the years 1953–5. He was an elected member of the Council of the Society in 1950–2, 1954–6 and 1962–3, became a Vice-President in 1957–8 and 1964 and President in 1965–7, clearly being one of the youngest to achieve this honour. Thus he has served the Council continuously from 1950 to the present day and has given freely of his time to the many Committees of Council. In all his Committee work he has always taken a positive role, has spoken his mind freely and has never suffered fools gladly. He came to the Presidency at a time when it was clear that changes in the Society's life were imminent and his wide experience of the Society's affairs was to prove invaluable. Two matters of major importance confronted him—accommodation and finance. Because of its expanding activities, the Society was outgrowing the office space available at Belgrave Square and after much hard work, arrangements were made for the Society to move to Savile Row as tenants of the Chemical Society. He initiated a study which led to the formulation of a salary structure for the permanent staff which will enable the Society to obtain the staff it requires to provide the improved services that members desire. He also initiated an O & M study by an independent consultant, of the activities of the Society's offices, which has proved of immense value. The new commitments were going to cost money and he made the financing of them his special concern; he realized that the actions necessary could only be put into effect over a period of years and in his address on retiring from the Presidency he surveyed in detail the working costs of the Society and pointed the way to future action. While especially concerned with the financial aspects of the Society's life, he did not neglect the analytical chemistry. He initiated detailed discussions of the activities of the existing committees, he laid plans for the continued expansion of the journals, and despite his many commitments, found time to attend many Section and Group meetings. He found particular pleasure in inaugurating the new North-East Section in May 1966, pleasure that was enhanced by his being able to present the first of the Society's gold medals for distinction in analytical chemistry to his old Chief, Mr. H. N. Wilson who, unfortunately, was to live only a few months after this happy day. Thus there is no doubt that the Society owes a special debt of gratitude to Albert Smales for his dedicated hard work on its behalf over many years, work that is still continuing.

He opened his Presidential Address to the Society for Analytical Chemistry on 3 March 1967 with a quotation from Graham Greene's novel "The Power and the Glory"—"Of course, before we know he is a saint, there will have to be miracles"—but in the course of his Address he felt unable to report any miracles. Anyone who in 1946 walked on the Berkshire Downs just to the west of the village of Harwell would have found a disused airfield, runways, hangars and grass and perhaps the ghosts of neolithic men strayed from the Icknield Way. If you walk along the same path today you will meet not ghosts but a very strong security fence and inside this you will find that one of the larger and most modern buildings is filled with the most up-to-date equipment for analytical work with a staff of more than 100. Twenty-one years of patient, purposeful and at all times arduous work has resulted in the creation of a large analytical organization of which any man would rightly be proud. We may not be ready to call Albert Smales a saint and perhaps here too no miracle in the accepted sense has been performed, but in the "analytical" sense his achievement is certainly something to be wondered at and worthy of any honour this volume can bring!

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THE IMPORTANCE OF SMALES'S WORK FOR IMPROVING THE QUALITY OF THE DATA OF GEOCHEMISTRY

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Summary—A critical account of Smales's contributions to the accumulation of data important in geochemistry.

IT IS noteworthy that one of Smales's first publications[1] dealt with the analysis of a mineral, monazite, a complex phosphate. Smales determined uranium and lead (both polarographically) and thorium (gravimetrically) for the purpose of estimating the geological age of the mineral. This early work on monazite provides an indication of the meticulous care which went into the analysis, a feature which has characterized all of Smales's subsequent work and which is so absolutely essential when analysing such complex substances as minerals, rocks and meteorites.

The encounter with the monazite evidently stimulated Smales's interest in the analysis of geological substances (minerals, rocks and ocean waters) as well as meteorites, and in the two decades following 1948, Smales and co-workers published some 32 papers connected with the analysis of these materials; in addition he edited[2] with L. R. Wager a book on analytical methods in geochemistry, which appeared in 1960.

The sheer number of publications is a clear indication of the contribution which Smales has made to the data of geochemistry and cosmochemistry. One particular aspect is, however, of unique importance; the excellence of the results. Such high quality analytical results are not only important in themselves, but they have in an indirect way helped to bring about an overall improvement in the quality of the data of geochemistry and the present paper will be concerned with Smales's contribution in these respects.

It will not be our purpose to survey and discuss all of the analytical work which Smales and his co-workers have carried out on geological materials and meteorites. Instead, three aspects will be chosen to illustrate the signal contribution which the Harwell analytical laboratory has made to geochemistry:

(i) work on the reference (standard) rocks granite G-1 and diabase W-1
(ii) investigations on the distribution of several of the rarer elements in rocks and minerals from Skaergaard, East Greenland, and
(iii) the production of high quality abundance data for meteorites.

REFERENCE ROCKS G-1 AND W-1

The usefulness of the reference rocks granite G-1 and diabase W-1 lies, in the first place, in the fact that they can serve as naturally occurring standards for optical, spectrochemical and X-ray fluorescent methods and thereby help to offset matrix effects, which for these methods of analysis can introduce serious error in the analytical determinations. In addition, these standard rocks together with others can serve for calibration and cross-checking purposes. In order to obtain optimum benefit from G-1 and W-1 or any other rock standard, the concentration of each element should be known with as much accuracy as possible, and in an endeavour to establish a "best" value a whole host of analytical techniques has been used.[3–6]

A little over a decade ago, this writer[7] discussed the principal analytical data of geochemistry and wrote, "Abundance data of high quality on several rare elements remains, however, the most serious need in geochemistry, and particular emphasis should be given to the introduction of highly accurate instrumental procedures such as radioactivation and isotope dilution." The great value of the reference rocks G-1 and W-1 for improving accuracy was emphasized in the same paper and the last sentence reads, "It is heartening to know that this object [accurate analysis of G-1 and W-1] is in view in the Harwell programme [Smales and co-workers] on the precision determination of rare elements in geological materials."

The concentrations of several elements in G-1 and W-1 have been estimated by Smales and co-workers, using for the most part neutron-activation methods. Among the elements estimated are Au, Co, Cs, Cu, In, Ni, Pd, Rb, Sc, Sr, Ta, V and W. For some of these elements the neutron-activation values are the first and only data available and in this respect are quite invaluable. Generally speaking, the neutron-activation data, whether obtained by Smales and co-workers or others, are often regarded as particularly important when attempts are made to ascertain the most accurate concentration for an element in G-1 and W-1. Nevertheless, in order to maintain proper perspective it should be recalled that other techniques may also provide reliable data; moreover, on occasion the neutron-activation data obtained by several workers may for one reason or another not agree satisfactorily. The results for gold and tantalum, and to a lesser extent gallium, are examples. Data on gold are given in Table I.

TABLE I.—ESTIMATED GOLD CONTENTS IN GRANITE G-1.
ALL DETERMINATIONS BY NEUTRON ACTIVATION

Au, *ppm*	Analysts
0·0095	Vincent and Smales[8]
0·0070	Crocket[9]
0·0045	Vincent and Crocket[10]
0·0046	Shcherbakov and Perezhogin[11]
0·0020	Baedecker and Ehmann[12]

Two determinations agree quite closely, but the range of all determinations (0·002–0·0095 ppm) is considerable. Neutron-activation values for tantalum range from 0·9 to 3 ppm.

However these discrepancies, which are purposely included to serve as a sobering reminder that some uncertainties may be found in any method of analysis, should not detract from the fact that analytical work carried out by Smales and co-workers on G-1 and W-1, as well as on other geological materials yet to be discussed, is invariably of very high quality.

The rare Group III element gallium is geochemically unique in one particular respect. Unlike that of most rare elements, the concentration of gallium varies very little in common aluminium-bearing rocks. The reason is that gallium is geochemically linked to the abundant element aluminium, the concentration of which itself varies only slightly in such common rocks as granite and basalt. The close geochemical association of aluminium and gallium is due to chemical and crystal-chemical similarities. Whereas, however, existing chemical procedures are sufficiently accurate to detect the small but petrologically important variations in the aluminium content (average content, 15% Al_2O_3), available techniques do not appear to be accurate enough to detect small variations in gallium content. The neutron-activation data (Table II) on diabase W-1 illustrate this point in part.

TABLE II.—NEUTRON ACTIVATION ESTIMATIONS OF THE GALLIUM CONTENT OF DIABASE W-1

Ga, *ppm*	Analysts
21	Morris and Chambers[13]
18·3	Vincent *et al.*[14]
16·5	Das and Desai[15]
19·5	Brunfelt, Johansen and Steinnes[16]

Although the agreement may be said to be reasonably good and there is little doubt that the results, together with numerous other determinations carried out by other methods, indicate strongly that the gallium concentration lies between 15 and 20 ppm, it is still not possible to establish a really precise value. In many igneous rocks, the gallium concentration varies between about 15 and 20 ppm. Such small variations in the gallium content or the aluminium/gallium ratio, may be geochemically significant—for comparing and distinguishing different types of basalt for example—and it is highly desirable that the neutron-activation methods initiated mainly by Smales and co-workers, or any other methods, can be so improved that very small differences can be precisely established.

ELEMENT DISTRIBUTION IN ROCKS OF THE SKAERGAARD INTRUSION

One of the best known and most thoroughly investigated suites of associated rocks on this planet is that which occurs in the form of a layered intrusion at Skaergaard, East Greenland. Wager and Deer[17] published a detailed account of the petrology of these rocks and Wager and co-workers (Wager and Mitchell,[18] for example) shortly thereafter studied the geochemical distribution of several rare elements in these rocks, using an optical spectrochemical method, more or less semi-quantitative in accuracy.

Shortly after his appointment to the Chair of Geology and Mineralogy at Oxford in 1951, Wager initiated further work on rocks and minerals of the Skaergaard intrusion. The close proximity of Oxford to Harwell greatly facilitated a long and fruitful co-operation between Wager and Smales; E. A. Vincent, then demonstrator in the Department of Geology and Mineralogy, and recently successor to the Chair held by the late Professor Wager, spent some time in the Harwell laboratories in the middle fifties learning the techniques of neutron-activation analysis.

In the post-1955 period, several significant papers on the geochemical distribution of some rare elements in Skaergaard and other rocks appeared. Each element was estimated by a neutron-activation procedure either by Smales himself or by someone trained in his laboratory. The examples discussed below serve to illustrate the importance of this work.

Whereas a considerable amount is known about the economic geochemistry of the noble metals gold and palladium, very little information is available on their distribution in common rocks, including those from layered intrusions. The concentration levels of palladium and gold in these rocks are ~0·1 and 0·001–0·01 ppm respectively. As a result of their observations on the gold distribution in Skaergaard rocks and minerals, Vincent and Smales[8] made the interesting and geochemically significant suggestion that a high proportion of gold was not chemically bound but dispersed as the free metal.

The comments above on the lack of knowledge of the general geochemistry of gold and palladium, applied to some extent a decade ago to the rare Group III element, indium. The concentration of this element in Skaergaard rocks and their separated minerals was investigated by Wager, van R. Smit and Irving,[19] by a neutron-activation technique. Relative to its concentration in the original magma (0·058 ppm), a three-fold enrichment was found in the ferrogabbros. Results of their work on the distribution of indium in some separated minerals from a hortonolite ferrogabbro are listed in Table III.

TABLE III.—ESTIMATED IN CONCENTRATION IN MINERALS FROM A SKAERGAARD HORTONOLITE FERROGABBRO

Mineral	In, *ppm*
Plagioclase	0·0032
Olivine	0·056
Pyroxene	0·18
Magnetite	0·16
Ilmenite	0·29

These results together with those for gold serve to illustrate the high sensitivity of neutron-activation analysis. The results in Table III also indicate quite clearly that indium tends to concentrate in pyroxene, magnetite and particularly ilmenite.

Though much is known about the composition of sulphide ore deposits, much less information has been available on the composition of sulphides from igneous rocks. Wager, Vincent and Smales[20] undertook such an investigation on sulphides from igneous rocks from Skaergaard. Many results for nickel, cobalt, copper, palladium and gold, all obtained by neutron-activation analysis, were included in this extensive and geochemically significant investigation.

TRACE ELEMENT ABUNDANCE DATA ON METEORITES

It is not easy to state categorically in which of the three geochemical applications discussed here Smales's contribution has been the most significant. In the opinion of this writer, the work of Smales and his co-workers on trace element abundance data in meteorites is perhaps the most noteworthy; moreover, much of this work, including the most important, is very recent. Most analyses have been carried out by neutron-activation techniques. The elements which have been investigated include rubidium, caesium, gallium, germanium, indium, arsenic, antimony, gold, palladium and rhenium. We will concern ourselves here with the most recent work (Fouché and Smales[21,22]).

In their first paper, Fouché and Smales[21] give data on the abundances and distribution of gallium, germanium and indium. They observed distinct fractionation of each of these elements between common (hypersthene and bronzite) chondrites, enstatite chondrites and the various types of carbonaceous chondrites. They also investigated the distribution of gallium, germanium and indium between the three principal phases (metal, sulphide and silicate) and confirmed the siderophile tendency of germanium. One significant and perhaps surprising conclusion is that germanium is quite strongly fractionated between the metal phases of the two sub-groups (hypersthene and bronzite) of the common chondites. In a general way, the composition of these chondrite types is very similar. Nevertheless, the average germanium content for the metal phase of the bronzite chondrites (64 ppm) was found to be only half that (125 ppm) of the metal phase in the hypersthene chondrites.

In their second study, Fouché and Smales[22] estimated gold, arsenic, palladium, rhenium and antimony in bronzite, hypersthene, enstatite and carbonaceous chondrites (all classes) and demonstrated conclusively that with the exception of antimony, the other elements were dominantly siderophile. They found that the concentration ranges of all these elements in the metal phase of chondrites were distinctly less than in the metal meteorites (irons), a significant conclusion.

Various observations on the fractionation of gold, arsenic, palladium, rhenium and antimony were made, one of which will be discussed here. Thus, whereas the average gold content in the metal phase from the bronzite chondrites was 1·37 ppm, the average in the metal phase from the hypersthene chondrites was 2·32 ppm. The difference is fairly small but probably quite significant and can only be detected if the analytical precision is high. The coefficient of variation for the neutron-activation techniques used by Fouché and Smales usually lies between 2 and 4%. Such reproducibility is highly significant for studies on the composition of meteorities, as much attention is currently being given to the problem of fractionation of the elements between different chondrite types. Fractionation may be extreme (thallium, lead and bismuth are examples), in which case techniques of moderate accuracy may be used. On the other hand, fractionation is often relatively small, as in the example of gold mentioned above, and better accuracy is required in order to detect it. Accuracy of of the highest order is, however, particularly required for examining the fractionation of *lithophile* element ratios (alkali metals, alkaline earths, silicon, *etc.*) in chondrites (Ahrens and von Michaëlis[23]), an aspect of fractionation which is important both for classifying chondritic meteorites (Van Schmus and Wood[24]) as well as for discussions on theories of their origin. It is desirable also to establish statistical relationships of lithophile element ratios between the different chondrite types and for this purpose accuracy of the highest order is required. For much of the fractionation work on meteorites a coefficient of variation of ~2% is required and it is gratifying that this precision is quite often approached and some times achieved. An enormous amount of work yet remains to be done in order to improve the accuracy of many analyses to this level. This is the challenge for the future and the work of Smales and his co-workers has been a great aid in progressing toward this goal.

Zusammenfassung—Eine kritische Würdigung der Verdienste von Smales um die Sammlung für die Geochemie wichtiger Daten.

Résumé—Un compte-rendu critique des contributions de Smales à l'accumulation de données importantes en géochimie.

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URANIUM AND THORIUM ABUNDANCES IN CHONDRITIC METEORITES

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Summary—Neutron-activation analyses for uranium and thorium are reported for 42 chondrite meteorite "falls" and 1 "find" covering 15 of the 20 Van Schmus–Wood chondrite types. The mean uranium and thorium abundances of the 5 chemical groups show a trend with C group ($U = 0{\cdot}012_0$ atoms/10^6 Si atoms, $Th = 0{\cdot}045_4$ atoms/10^6 Si atoms, $Th/U = 3{\cdot}7_8$) > H, L and LL groups ($U = 0{\cdot}008_3$, $Th = 0{\cdot}028_0$, $Th/U = 3{\cdot}4_5$) > E group ($U = 0{\cdot}005_9$, $Th = 0{\cdot}021_8$, $Th/U = 3{\cdot}6_9$). With the possible exception of the C3 chondrites, the mean abundances for each petrologic type within a given chemical group are identical.

THE chondritic meteorites form by far the largest number of observed falls[1] and generally exhibit a remarkable uniformity of composition, particularly with respect to the major components.[2,3] At the trace element level, however, it has been found that some elemental abundances show wide variations between the various chondritic classes,[4,5] and this has led to widespread interest in the determination of the rarer elements. Comparisons of chondritic atomic abundances (normalized to 10^6 Si atoms) with those observed in the solar photosphere have shown a general similarity, particularly in the case of the carbonaceous chondrites.[5] Chondrite analyses have therefore played a large part in the construction of charts of "cosmic" (meaning solar system) abundances,[6,7] which in turn have had a fundamental role in the development of theories of nucleosynthesis.[8–10]

Uranium and thorium are of considerable interest in cosmochemistry because of their special place in the chart of the nuclides and in the periodic table. In nucleosynthesis the wide gap between the heaviest stable nuclides and these two elements can only be bridged by neutron capture on a rapid scale, that is, the *r* process of Burbridge *et al.*[8] The measured abundances of uranium and thorium provide a rigorous test of the nuclear laws used in arriving at calculated solar system abundances.[11,12] The instability of thorium-232, uranium-235 and uranium-238 to alpha-decay leads to changes in their relative abundances with time. These variations have been applied to a discussion of the time-scale of nucleosynthesis or "cosmochronology" by Fowler and Hoyle.[13] The significance of several new neutron-activation analyses of carbonaceous chondrites for uranium and thorium, in these largely theoretical studies of nucleosynthesis and nuclear cosmochronology, has been discussed in detail recently,[14] and therefore these topics will not be dealt with again in the present work.

The general similarities in geochemical behaviour of uranium and thorium in igneous rocks have been discussed widely and are largely due to the almost identical

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radii of the quadrivalent ions. On the other hand the considerable fractionation between the two elements in certain sedimentary environments can be attributed to the ease with which uranium is oxidized to the sexivalent state and the solubility of the uranyl ion in an aqueous environment under a wide range of conditions.

The degree of oxidation in the chondritic meteorites varies from the carbonaceous chondrites [containing high iron(III) and hydroxide ion contents together with carbonates and sulphates], to the enstatite chondrites, in which iron is completely reduced to metal containing a few per cent of elemental silicon in solution, and in which elements such as calcium, chromium and titanium occur largely as sulphides rather than oxides. A study of the variation of uranium and thorium chondritic abundances both absolutely and relative to each other would be of considerable importance to theories of the chemical evolution of the meteorites. The object of the present work was to provide a large number of analyses for these elements, covering all the chondrite classes for which representative samples could be obtained.

Previous uranium and thorium determinations in chondrites

Although several attempts were made in the early 1950's to measure the uranium abundance of chondritic meteorites, it was not until the publication of the neutron-activation analyses by Hamaguchi, Reed and Turkevich[15] and, independently, by Wänke and co-workers,[16–18] that a consistent value of about $10^{-6}\%$ (10 ppM*) uranium emerged for the ordinary chondrites. In fairness to earlier investigators it should be mentioned that a similar value had previously been obtained by fluorimetric methods for the Akaba chondrite,[19] and by stable-isotope dilution for the Modoc chondrite.[20] More recently neutron-activation results have been reported for uranium in the rarer enstatite and carbonaceous chondrites.[4,21–24] Although, for various reasons, the precision of these later measurements was not as good as for the ordinary chondrites, they established that there was no large scale fractionation as has been observed with certain other trace elements. Further analyses for uranium by a new technique of delayed neutron counting have been published.[24] The sensitivity of this method is not as great as that of conventional neutron-activation techniques; however, the results quoted for ordinary chondritic falls are consistent with the accepted values.

There are very few reliable thorium determinations available for chondritic meteorites, and then only for ordinary chondrites.[23,26] These were all measured by a neutron-activation technique based on protactinium-233.

It should be noted that in no case were thorium and uranium determined in the same sample, though samples from the same fall have been analysed for both elements in a few instances. As has been pointed out by Greenland and Lovering, it is important, when studying the co-variance of trace elements in samples as macroscopically heterogeneous as chondrites, that the analyses should be carried out on the same sample. In the present work therefore a neutron-activation method was developed in which both elements were determined simultaneously.[27]

ANALYTICAL METHOD

Sample preparation

Where possible, samples were taken from the interior portion of the specimen, particular care being taken that they should be as far as practicable from the fusion crust whenever this was present.

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* ppM = parts per milliard.

For large specimens the outer parts were removed with a large screw-driven steel wedge, which was particularly useful for the harder stones. With practice it was possible to obtain rectangular pieces of 1–2 cm edge, with completely fresh surfaces, comprising more than half the weight of specimen used. Where the sample available was very small or irregular in shape the use of the wedge became prohibitively extravagant, and outer surfaces were carefully chipped away with a pair of steel side-cutters kept exclusively for this purpose. Frequently a combination of the two techniques was used.

The fresh pieces thus obtained were crushed to powder. If the sample was particularly hard it was first broken down in a steel percussion mortar to small pieces about 3–4 mm across. Samples were crushed to less than 100-mesh size in an agate mortar. Specimens containing no metal fragments, or in which the metal particles were very small, were sieved through a 100-mesh Spex nylon sieve. Otherwise the samples were crushed until the silicate phase appeared suitably reduced in size. No efforts were made to break down the metal fragments further. The samples were well mixed and quartered. Only in the case of the chondrite Farmington were metal fragments extracted before analysis. When this specimen was prepared, three or four large tabular pieces of metal were found which would have been very difficult to sample properly. These were removed and weighed, and the results of the analyses on the remaining powder were corrected accordingly. It was assumed that the uranium and thorium content of the metal removed from Farmington was negligible. The technique of crushing the metal-bearing samples under acetone at low temperature below the embrittlement point of the nickel–iron[28] was not used because of the increased possibility of contamination. Portions of the prepared chondrite (usually 0·1–0·2 g) were weighed into clean dry 4-mm diameter silica ampoules, which were sealed before irradiation.

Preparation of standards

Standards were prepared from analytical grade uranyl nitrate and thorium nitrate. The uranyl salt was standardized gravimetrically by the preparation of stoichiometric U_3O_8.[29] Thorium nitrate was standardized by titration with EDTA, with Xylenol Orange as the indicator.[30] Dilute standard solutions were made up by weight in dilute nitric acid to give a final concentration of uranium and thorium between about 20 and 100 μg/g of solution. Standards were prepared for irradiation by spiking Johnson-Matthey Specpure silicon dioxide with known weights of dilute standard solution. About 20 mg of silicon dioxide were weighed into a clean dry ampoule, a similar weight of solution was added and the ampoule was weighed again. The ampoule was centrifuged to ensure that all the solution was brought in contact with the silicon dioxide. The standards were dried overnight at 80° and then for several hr at 110°. The ampoules were then sealed.

Neutron irradiation

Batches for irradiation usually consisted of six sample ampoules and two standards. Irradiations were carried out generally in the high-flux position of the "self-serve" facility of the HIFAR reactor at the Australian Atomic Energy Commission Research Establishment, Lucas Heights, N.S.W. The available thermal neutron flux was nominally 9×10^{12} n.cm^{-2}.sec^{-1}, and the duration of irradiation generally one week. The characteristics of the neutron spectrum, and the effect of this on possible interfering reactions have been discussed in detail previously.[27] The analyses were based on the reactions:

$$\begin{array}{ll} {}^{238}\mathrm{U}(\mathrm{n}, \gamma){}^{239}\mathrm{U} & (\sigma = 2{\cdot}7 \text{ barns}) \\ \quad\Big\downarrow\ t_{1/2} = 23{\cdot}5 \text{ min} & \\ \quad {}^{239}\mathrm{Np}\ (t_{1/2} = 2{\cdot}36 \text{ day}) & \\ {}^{232}\mathrm{Th}(\mathrm{n}, \gamma){}^{233}\mathrm{Th} & (\sigma = 7{\cdot}3 \text{ barns}) \\ \quad\Big\downarrow\ t_{1/2} = 22{\cdot}4 \text{ min} & \\ \quad {}^{233}\mathrm{Pa}\ (t_{1/2} = 27{\cdot}0 \text{ day}) & \end{array}$$

The fission reaction for the determination of uranium was not used because of the greater sensitivity and specificity of neptunium-239. The use of a suitable fission product would otherwise have been more convenient in that carriers could have been used. Carrier-free chemistry was necessarily involved in the thorium determination.

Radiochemical procedures

The detailed radiochemical separations have been described previously[27] and will only be outlined here.

After irradiation the samples were transferred to zirconium crucibles and known amounts of the long lived α-emitters protactinium-231 and neptunium-237 were added as tracers. The meteorites were fused with sodium peroxide and after cooling the fusion cake was dissolved in water. The hydroxides, with which neptunium and protactinium were co-precipitated, were centrifuged down, and then fumed with hydrofluoric and perchloric acids. The residue was dissolved in 8*M* hydrochloric acid–0·5*M* hydroxylamine hydrochloride and put on a small anion-exchange column in the chloride form. Neptunium was eluted by 5·9*M* hydrochloric acid and protactinium by 3·8*M* hydrochloric acid.

Neptunium was further purified by co-precipitation with lanthanum fluoride, then by solvent extraction. The extraction procedure was based on the method described by Maeck *et al.*[31] in which neptunium(VI) is extracted into isobutyl methyl ketone (IBMK) from an acid-deficient aluminium nitrate solution containing tetrapropylammonium nitrate. It is then back-extracted into iron(II) chloride solution and extracted into 2-thenoyltrifluoroacetone (TTA). In our procedure the acid-deficient extraction step was repeated before going on to the final TTA extraction.

Protactinium was extracted into di-isobutylcarbinol (DIBC) from a 6*M* hydrochloric acid solution containing oxalic acid and tin(II) chloride,[32] then back-extracted into 1*N* sulphuric acid. The strip solution was made 6*M* in hydrochloric acid and protactinium extracted into IBMK. It was back-extracted from the ketone phase into 2*M* hydrochloric acid, from which it was finally extracted into TTA.

Sources for both neptunium and protactinium were prepared on stainless steel discs by evaporation of the TTA extract, peripheral heating being used. Activities of protactinium-233 and neptunium-239 were measured by beta-counting and recoveries determined by alpha-counting.

Radioactivity measurements were usually made with a Beckman WIDEBETA I automatic counter. This instrument is capable of measuring alpha- and beta-activities simultaneously, which had the advantage that a large number of alpha-counts could be accumulated while beta decay-curves were being followed.

The alpha activity of the tracers made a measurable contribution to the beta-count rate for which a correction had to be made. In the case of protactinium-231 the apparent beta: alpha ratio remained constant over a period of several months, but with neptunium-237 the ratio increased owing to the growth of protactinium-233 daughter. It was necessary, therefore, to construct an empirical neptunium-237 growth curve to correct the neptunium-239 beta-count rate. The time of the second acid-deficient IBMK extraction was taken as the zero point of the protactinium-233 growth. A small correction also had to be made to the protactinium-233 activity to allow for the activity of this nuclide introduced with the neptunium-237 tracer.

Radiochemical purity of the sources was checked by following beta decay-curves for at least two half-lives. Where possible, additional checks were made by examination of gamma-spectra and construction of beta-absorption curves. The alpha-energies of some sources were checked with a Frisch gridded ion chamber connected to a slow Wilkinson 100-channel pulse-height analyser.

RESULTS AND DISCUSSION

Altogether, 59 samples taken from 42 observed falls and one find (Bencubbin) were analysed. Details of the sources from which specimens were obtained are given in Appendix A. In all cases duplicate analyses were made on each sample, with the exception of Warrenton where the duplicate measurement was lost by misadventure. A critical evaluation of the results (Table I) led to the rejection of certain analyses. Generally it was possible to make objective decisions about the acceptance or rejection of results. For example, in the case of the ordinary chondrites, the repeat analyses on Farmington, Forest Vale, Homestead, Mount Browne and Zhovtnevyi provided strong evidence that the original samples were contaminated. It should be noted in passing, that for Mount Browne and Zhovtnevyi, only uranium contamination was significant, and the repeat thorium analyses are in very good agreement with the original values. No further sample of Mocs was available for analysis, but a single uranium value of 11 ppM reported by Goles and Anders[21] indicates that our sample was probably contaminated and our analyses for this sample were rejected. The case is rather more complicated when the results for Bjurböle are considered. The powder for this analysis was carefully prepared from a large specimen, and from this point of view should be considered a good sample. On the other hand this meteorite was recovered after falling through ice into a lake. Because of the very porous nature of Bjurböle it is possible that water, and perhaps even some fine clay fractions, may have penetrated

Table I.—Uranium and thorium abundances in chondrites

Class	Fall	Uranium, *ng/g*		Thorium, *ng/g*		Th/U
C1	Alais	10·0 ± 0·3 9·6 ± 0·3	9·8	37·5 ± 0·8 39·8 ± 0·8	38·7	4·0
C1	Ivuna I	11·4 ± 0·7 13·8 ± 0·8	12·6	28·4 ± 0·5 29·3 ± 0·5	28·9	2·3
	Ivuna II	7·4 ± 0·2 7·6 ± 0·2	6·5	26·4 ± 0·6 29·0 ± 0·6	27·7	3·7
	Ivuna III	8·2 ± 0·3 8·3 ± 0·3	8·3	29·2 ± 1·2 30·2 ± 1·2	29·7	3·6
C1	Orgueil IA	19·5 ± 0·5 28·8 ± 0·4	2·42	59·5 ± 1·5 70·0 ± 1·8	64·1	2·7
	Orgueil IB	26·2 ± 0·3 21·8 ± 0·5	24·0	76·8 ± 1·2 64·8 ± 1·0	70·8	2·9
	Orgueil II	17·2 ± 0·4 19·5 ± 0·4	18·3	40·7 ± 0·6 40·5 ± 0·5	40·6	2·2
	Orgueil IV	8·1 ± 0·2 7·7 ± 0·2	7·9	33·2 ± 0·7 34·4 ± 0·8	33·8	4·3
C1	Tonk	11·5 ± 0·3 9·8 ± 0·3	10·7	31·0 ± 0·7 31·6 ± 0·7	31·3	2·9
C2	Cold Bokkeveld	11·3 ± 0·2 10·6 ± 0·1	11·0	39·8 ± 0·4 40·1 ± 0·5	40·0	3·6
C2	Mighei	16·1 ± 1·5 17·7 ± 2·7	16·9	45·7 ± 0·8 45·5 ± 0·8	45·6	2·7
C2	Mokoia	14·4 ± 0·4 13·5 ± 0·4	14·0	60·2 ± 1·8 60·8 ± 1·8	60·5	4·3
C2	Murray	11·0 ± 0·2 11·6 ± 0·4	11·3	45·2 ± 0·5 45·6 ± 0·7	45·4	4·0
C2	Nawapali	10·3 ± 0·3 11·3 ± 0·3	10·8	39·1 ± 1·6 37·7 ± 1·5	38·4	3·6
C2	Renazzo II	11·8 ± 0·3 11·9 ± 0·3	11·8	40·3 ± 0·8 41·3 ± 0·9	40·8	3·5
	Renazzo III	11·4 ± 0·3 10·8 ± 0·3	11·1	41·7 ± 1·7 42·3 ± 1·7	42·0	3·8
C2	Staroe Boriskino	10·2 ± 0·3 11·9 ± 0·3	11·1	39·2 ± 0·8 38·2 ± 0·8	38·7	3·5
C3	Bencubbin (find) (Carbonaceous inclusion)	17·6 ± 1·9 20·4 ± 2·2	19·0	76·0 ± 1·5 75·7 ± 1·5	75·9	4·0
C3	Lancé	23·1 ± 1·0 17·7 ± 0·7	20·4	104 ± 2 131 ± 2	118	5·8
C3	Warrenton	18·3 ± 1·1		79·3 ± 24·3		4·3
C4	Karoonda	12·5 ± 0·3 14·8 ± 0·4	13·7	59·9 ± 2·1 53·3 ± 1·5	56·6	4·1
E4	Abee	8·8 ± 0·2 9·3 ± 0·2	9·0	28·7 ± 0·6 31·7 ± 0·6	30·0	3·3
	Indorch	10·5 ± 0·6 11·0 ± 0·7	10·8	28·5 ± 0·5 28·9 ± 0·5	28·7	2·7
E5	St. Mark's II	7·0 ± 0·1 7·4 ± 0·1	7·2	29·4 ± 0·4 30·2 ± 0·4	29·8	4·1
	St. Mark's III	8·3 ± 0·2 9·1 ± 0·2		30·2 ± 0·4 31·8 ± 0·6	31·0	3·6
E6	Hvittis	6·2 ± 0·2 6·2 ± 0·3	6·2	29·2 ± 0·6 31·7 ± 0·6	31·1	5·0
E6	Khairpur II	14·3 ± 0·3 17·8 ± 0·3	16·1	44·4 ± 0·7 37·6 ± 0·6	41·0	2·5
E6	Pillistfer	6·1 ± 0·1 5·8 ± 0·1	5·9	42·5 ± 0·7 41·3 ± 0·7	41·9	7·1

TABLE 1. (*Contd.*)

Class	Fall	Uranium, *ng/g*		Thorium, *ng/g*		Th/U
H4	Forest Vale II	9·4 ± 0·2 13·2 ± 0·2	11·3	41·6 ± 0·6 41·9 ± 0·6	41·8	3·7
H4	Ochansk	10·7 ± 0·2 10·9 ± 0·3	10·8	39·2 ± 0·7 42·7 ± 0·9	40·9	3·8
H5	Allegan	11·4 ± 0·2 10·0 ± 0·1	10·7	41·8 ± 0·7 36·5 ± 0·5	39·2	3·7
	Beardsley	10·2 ± 0·3 10·4 ± 0·2	10·3	36·7 ± 0·3 35·9 ± 0·5	36·3	3·5
	Pultusk	12·0 ± 0·2 13·0 ± 0·2	12·5	39·2 ± 0·7 42·2 ± 0·6	40·7	3·3
	Richardton	10·8 ± 0·4 10·7 ± 0·2	10·7	27·6 ± 0·7 31·5 ± 0·6	29·6	2·8
H6	Mount Browne II	12·9 ± 0·2 11·4 ± 0·2	12·2	38·8 ± 0·6 42·8 ± 0·7	40·8	3·3
H6(?)	Zhovtnevyi	12·6 ± 0·2 16·5 ± 0·3	14·6	41·6 ± 0·6 42·4 ± 0·7	42·0	2·9
L3	Khohar	12·7 ± 0·3 11·8 ± 0·4	12·3	42·3 ± 0·6 44·7 ± 0·4	43·5	3·5
L5	Farmington II	11·0 ± 0·1 11·0 ± 0·1	11·0	38·4 ± 0·6 38·4 ± 0·6	38·4	3·5
L5	Homestead II	11·4 ± 0·2 11·6 ± 0·4	11·5	38·3 ± 0·6 42·1 ± 0·6	40·2	3·5
	Knyahinya	20·3 ± 0·6 17·7 ± 0·5	19·0	48·3 ± 0·5 49·9 ± 0·6	49·1	2·6
L6	Holbrook	12·5 ± 0·4 14·8 ± 0·4	13·7	40·5 ± 0·8 45·9 ± 0·9	43·2	3·2
	Perpeti	9·6 ± 0·3 11·0 ± 0·2	10·3	39·7 ± 0·6 40·3 ± 0·6	40·0	3·9
	St. Michel	15·1 ± 0·3 15·9 ± 0·2	15·5	43·5 ± 0·9 44·6 ± 0·8	44·0	2·8
LL3	Chainpur	14·1 ± 0·8 13·8 ± 0·8	13·9	42·7 ± 0·7 43·8 ± 0·7	43·3	3·1
	Ngawi	11·2 ± 0·2 9·8 ± 0·4	10·5	42·0 ± 0·6 43·9 ± 0·6	43·0	4·1
LL6	Bandong	13·0 ± 0·3 13·2 ± 0·4	13·1	49·1 ± 0·9 50·0 ± 0·9	49·6	3·8
	Benares	12·7 ± 0·3 11·4 ± 0·2	12·1	41·9 ± 0·6 45·1 ± 0·7	43·5	3·6
	"Bialystok"	12·5 ± 0·2 12·4 ± 0·2	12·5	47·9 ± 0·6 52·1 ± 0·7	50·0	4·0

the stone.[33] The high uranium and thorium values found may therefore be due to terrestrial contamination, despite the care taken in preparation of the sample. It should be borne in mind, however, that Bjurböle is an unusual meteorite in many ways, and the possibility that the present uranium and thorium analyses may truly reflect the preterrestrial abundances cannot be completely rejected on the evidence at present available.

The justification for the rejection of the enstatite chondrite samples Khairpur I and St. Mark's I is clear cut. In both samples, very high abundances were found, whereas repeat analyses were at a level comparable with or below the ordinary chondrite abundances. Another sample of St. Mark's contaminated with uranium has been found by Goles and Anders.[21] A fission track study of St. Mark's[34] revealed localized areas of very high uranium concentration, indicating that either the meteorite was contaminated, or that minerals such as zircon or some phosphates were sporadically distributed throughout the meteorite.

Of the carbonaceous chondrites, only Renazzo I shows a really good cause for rejection. The repeat analyses on two further samples gave results clearly compatible with other C2 chondrites. The Orgueil samples presented a much more confused picture. The original sample analysed, IA, gave very much higher values than those obtained by Reed *et al.*,[4] though it should be noted that for various reasons those authors considered that their uranium values were not as reliable as their earlier work.[15] We prepared a second sample from further pieces of the Orgueil I specimen and obtained virtually identical results with consistent thorium/uranium ratios for each determination. It should be stressed that when a similar procedure was carried out with some of the suspect ordinary chondrites (for example Forest Vale, Homestead, Mount Browne and Zhovtnevyi) the second sample gave much lower results. It is probably fair to say that IA and IB are good values for that particular specimen of Orgueil. Orgueil II gave somewhat lower results, though the uranium values were close to the lower value of sample IA. Sample IV uranium was in good agreement with the value of Reed *et al.*[4] In both samples II and IV the thorium/uranium ratios for each of the duplicate analyses were internally consistent. This was not the case however for sample III. Here, though the uranium values appeared in accord with those of other samples, one of the thorium values was much higher than even the highest value found in sample IA or IB. The ratios in III were widely discrepant. In the other Cl analyses, as will be discussed later, it was found that uranium and thorium were quite strongly correlated. It was therefore concluded that at least one of the Orgueil III samples was contaminated with thorium, and the sample was rejected.

The results for the C3 chondrites were also regarded with a certain amount of suspicion, especially Lancé. Not only were the results rather high, but the samples were not specially prepared for the present investigation. Reed[22] analysed a sample of Lancé and found 28 ppM uranium. Later Reed and Allen[23] reported 7 ppM for another sample. It would seem therefore that Lancé is rather variable in at least uranium. Our values for uranium fell between the two published values and were therefore accepted. It is felt however that in a discussion of abundances our results for Bencubbin, Lancé and Warrenton should be regarded with a certain reserve until further analyses are made on more carefully controlled samples.

The results regarded as acceptable are summarized in Table I. The chondrites are grouped according to the "chemical-petrological" classification of Van Schmus and Wood.[35] Some of the results have been published previously.[14,36] The rejected analyses are given in Appendix B for the sake of completeness.

A comparison of the acceptable results from the present work and values reported in other studies can be made by reference to Table II. Rejected values are also included, in parentheses.

It can be seen that in general the agreement is good, with our results being consistent with at least some of the previous results for each fall. It might be argued that

TABLE II.—COMPARISON OF URANIUM AND THORIUM ANALYSES IN CHONDRITES

Meteorite	Uranium, *ng/g* Previous work	Uranium, *ng/g* This work	Thorium, *ng/g* Previous work	Thorium, *ng/g* This work
Abee	11(b), 15(c)	9		
Allegan	12(a)	11		
Beardsley	11(e)	10	43(i)	36
Farmington	18(h)	11 (92)		
Holbrook	11, 14(g), 16(b)	14	90(i), 38(j)	43
Hvittis	2(a)	6		
Indarch	16(b), 9(c)	11		
Ivuna	8, 7(a)	13, 7, 8		
Lancé	28(d), 7(a)	20		
Mighei	16(b), 15(c), 8(a)	17		
Mocs	11(c)	(84)		
Murray	20(c)	11		
Orgueil	8(b), 6(a)	24, 18, 8 (15)		
Pultusk	12(f), 12(e)	13		
Richardton	11, 13(g), 15(h)	11	38(j)	30
St. Mark's	9, (120)(b)	7, 9 (3170)		

(a) Reed and Allen[23]
(b) Reed *et al.*[4]
(c) Goles and Anders[21]
(d) Reed[22]
(e) König and Wänke[18]
(f) Ebert *et al.*[17]
(g) Hamaguchi *et al.*[15]
(h) Amiel *et al.*[24]
(i) Bate *et al.*[25]
(j) Bate *et al.*[26]

the criterion used for rejection depended in part on previous results, and therefore the comparison is not strictly valid. This is not the case, however, as the only sample rejected mainly by comparison with published results was Mocs, and this sample was suspect for other reasons (see Appendix B). It is probably fair to say, then, that the overall comparison of results shows no particular analytical bias when compared with other methods, and that the precision is generally much better. Other comparative studies of the accuracy of our method applied to terrestrial rocks[27,37,38] have also proved it satisfactory.

Fractionation in the Van Schmus–Wood chondrite group

In order to compare realistically the abundances of uranium and thorium in different groups it is necessary to convert the results of the analyses into atomic abundances. By convention it is customary to normalize to 10^6 atoms of silicon and this practice will be followed here. It should be noted that there is evidence to suggest that it may be preferable to normalize with respect to titanium,[5] but so far this innovation has not been generally adopted. Table III lists uranium and thorium atomic abundances calculated relative to 10^6 atoms of silicon. Only the means of the duplicate analyses are reported in Table III but in the calculation of average abundances and standard deviations for each group all determinations have been used. To facilitate discussion of the variation or uranium and thorium in the light of the Van Schmus–Wood classification the results have been grouped accordingly and the averages summarized in Table IV.

Fractionation between chemical groups

The last column of Table IV lists the mean abundances of uranium and thorium in each chemical group. It can be seen that the abundances of both elements decrease

TABLE III.—ATOMIC ABUNDANCE OF URANIUM AND THORIUM IN CHONDRITES, RELATIVE TO SILICON

Van Schmus–Wood Classification	Fall	Atoms/10^6 Si atoms U	Th
C1	Alais	0·012	0·048
	Ivuna	0·011 ± 0·003	0·033 ± 0·002
	Orgueil	0·018 ± 0·009	0·053 ± 0·019
	Tonk	0·012	0·036
C1	Weighted Mean	0·013 ± 0·006	0·043 ± 0·013
C2	Cold Bokkeveld	0·010	0·038
	Mighei	0·015	0·043
	Mokoia	0·011	0·047
	Murray	0·010	0·041
	Nawapali	0·010	0·037
	Renazzo	$0{\cdot}008_5 \pm 0{\cdot}000_4$	$0{\cdot}031_7 \pm 0{\cdot}000_6$
	Staroe Boriskino	0·010	0·036
C2	Weighted Mean	0·011 ± 0·002	0·038 ± 0·004
C3	Bencubbin	0·015	0·059
	Lancé	0·016	0·092
	Warrenton	0·013	0·059
C3	Mean	0·015 ± 0·002	0·072 ± 0·020
C4	Karoonda	0·010	0·044
E4	Abee	0·006	0·020
	Indarch	0·0071	0·019
E4	Mean	$0{\cdot}006_5 \pm 0{\cdot}000_6$	0·020 ± 0·001
E5	St. Mark's	$0{\cdot}005_2 \pm 0{\cdot}000_6$	$0{\cdot}020_4 \pm 0{\cdot}000_7$
E6	Hvittis	0·004	0·019
	Khairpur	0·010	0·025
	Phillistfer	0·004	0·026
E6	Mean	0·006 ± 0·003	0·023 ± 0·004
H4	Forest Vale	0·008	0·030
	Ochansk	0·008	0·030
H4	Mean	0·008 ± 0·001	0·030 ± 0·001
H5	Allegan	0·008	0·029
	Beardsley	0·007	0·027
	Pultusk	0·009	0·030
	Richardton	0·008	0·022
H5	Mean	0·008 ± 0·001	0·027 ± 0·004
H6	Mount Browne	0·009	0·030
	Zhovtnevyi	0·010	0·028
H6	Mean	0·009 ± 0·001	0·029 ± 0·002
L3	Khohar	0·008	0·030
L5	Farmington	0·007	0·026
	Homestead	0·007	0·027
	Knyahinya	0·012	0·031
L5	Mean	0·009 ± 0·002	0·028 ± 0·003
L6	Holbrook	0·009	0·028
	Perpeti	0·007	0·027
	St. Michel	0·010	0·029
	Mean	0·008 ± 0·002	0·028 ± 0·002
LL3	Chainpur	0·009	0·028
	Ngawi	0·007	0·028
	Mean	0·008 ± 0·001	0·028 ± 0·001
LL6	Bandong	0·008	0·032
	Benares	0·007	0·028
	"Bialystok"	0·008	0·031
	Mean	$0{\cdot}007_7 \pm 0{\cdot}000_4$	0·030 ± 0·002

TABLE IV.—URANIUM AND THORIUM ATOMIC ABUNDANCES IN CHONDRITES CLASSIFIED ACCORDING TO VAN SCHMUS–WOOD SCHEME

Chemical group	Petrologic type 1	2	3	4	5	6	Chemical group means, *atoms/10^6 Si atoms*
E	*	*	†	U:0·006$_5$ Th:0·020	U:0·005$_2$ Th:0·020$_4$	U:0·006 Th:0·023	U:0·005$_9$ Th:0·021$_8$ Th/U = 3·69
C	U:0·013 Th:0·043	U:0·011 Th:0·038	U:0·015 Th:0·072	U:0·010 Th:0·044	*	*	U:0·012$_0$ Th:0·045$_4$ Th/U = 3·78
H	*	*	†	U:0·008 Th:0·030	U:0·008 Th:0·027	U:0·009 Th:0·029	U:0·008$_8$ Th:0·028$_8$ Th/U = 3·41
L	*	*	U:0·008 Th:0·030	†	U:0·009 Th:0·028	U:0·008 Th:0·028	U:0·008$_5$ Th:0·028$_1$ Th/U = 3·31
LL	*	*	U:0·008 Th:0·028	†	†	U:0·0077 Th:0·030	U:0·007$_7$ Th:0·029$_1$ Th/U = 3·78

* Unpopulated.
† Representatives of these groups not available for study.

in the order C > H, L, LL > E, a trend that was indicated in a previous study.[36] Similar trends have been observed for other oxyphilic trace elements, notably yttrium.[39] Ahrens[40] has shown that a similar fractionation has taken place, with respect to silicon, for the major elements magnesium, aluminium and calcium. If the uranium and thorium atomic abundances found in the present study are multiplied by the Si/Al or Si/Ca ratios for each chondrite as listed by Ahrens, the fractionation trends virtually disappear. This is particularly true when the uranium abundances are normalized to aluminium. The major exception is the C3 chondrite Lancé, which still appears enriched in thorium and to a lesser extent uranium, even when recalculated on the basis of aluminium or calcium. There is little fractionation between uranium and thorium amongst the Van Schmus–Wood chemical groups. This is best shown by inspection of the values for the thorium/uranium ratios which are very nearly constant. Attention should be drawn to the opposite conclusion reached by us in a preliminary report,[36] when it seemed that the ratio varied inversely with uranium abundance. This earlier conclusion can now be seen to be in error.

If the average uranium and thorium atomic abundances for each chemical group are plotted logarithmically, as in Fig. 1, the five points define a regression line with a slope of 1·01, indicating a virtually constant thorium/uranium ratio: the value of the ratio at the intercept equivalent to a uranium abundance of 0·01 atoms per 10^6 silicon atoms is 3·60. This figure is in substantial agreement with the ratio of 3·8 derived for ordinary chondrites by Murthy and Patterson[41] from their ^{208}Pb/^{204}Pb–^{206}Pb/^{204}Pb isochron.

Fractionation within chemical groups

Inspection of Table IV reveals that it is only within the C chemical group that the mean uranium and thorium abundances for each petrological group show any apparent

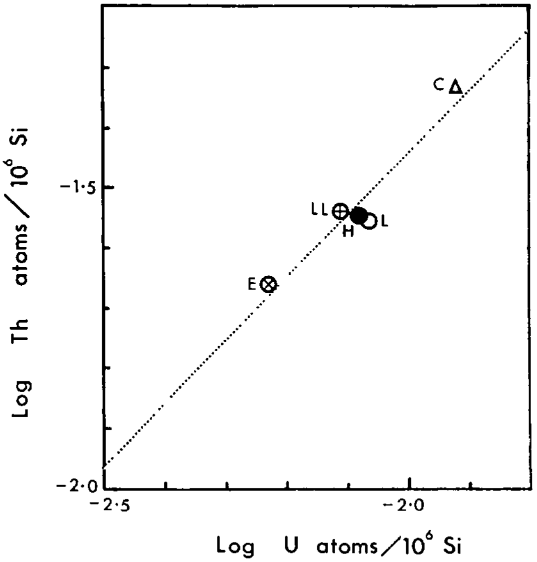

FIG. 1.—Logarithmic plot of thorium and uranium atomic abundances relative to 10^6 Si atoms for the five Van Schmus–Wood chondrite chemical groups.

variation. The ordinary chondrites show remarkable uniformity, not only within each chemical group but also between them. There are no systematic variations with petrological group such as were observed with indium abundances in the L group chondrites,[42] presumably a reflection of the different geochemical affinities of uranium and thorium and this element. It is significant that the oxyphile element caesium, the abundance of which varies almost as much as that of indium within the ordinary chondrites,[43] shows no similar systematic variation with increasing metamorphism between petrological groups.

Although there is remarkable uniformity between the mean abundances of uranium and thorium for the petrological groups within the H, L and LL chemical groups, individual chondrites show some variations. This is most noticeable in the L group, (see Fig. 2) where uranium and thorium abundances are strongly correlated ($r = 0{\cdot}79$). The correlation is not significant in the H group ($r = 0{\cdot}25$) or the LL group ($r = 0{\cdot}06$).

The E petrological groups exhibit uniform uranium and thorium abundances, and it is only within the E6 group that there is any large variation of abundance between the individual chondrites. There is no correlation of abundance with petrological group number, and the variations of uranium and thorium abundance between the members of the E group analysed in this work are not significantly correlated ($r = 0{\cdot}09$). In a previous publication[14] it has been shown that the uranium and thorium abundances of groups C1 and C2 are statistically indistinguishable at the 95% confidence level. A similar comparison of the C1 and C2 groups with C4 is not possible as only one duplicate analysis is available for that group, but it can be seen that the abundances are very close to those of the C1 and C2 groups. A test of significance of the difference between the means of the C1 and C3 group indicates that though the uranium abundances are identical at the 95% confidence limit, the thorium abundances are significantly different. A similar test of the means of the C2 and C3 groups shows

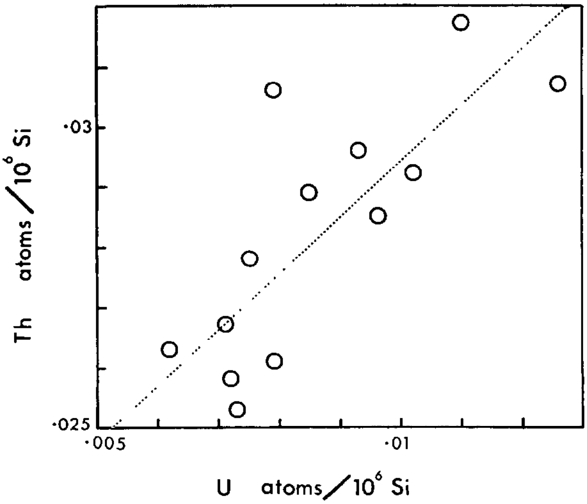

FIG. 2.—Thorium and uranium atomic abundances relative to 10^6 Si atoms for the L group chondrites.

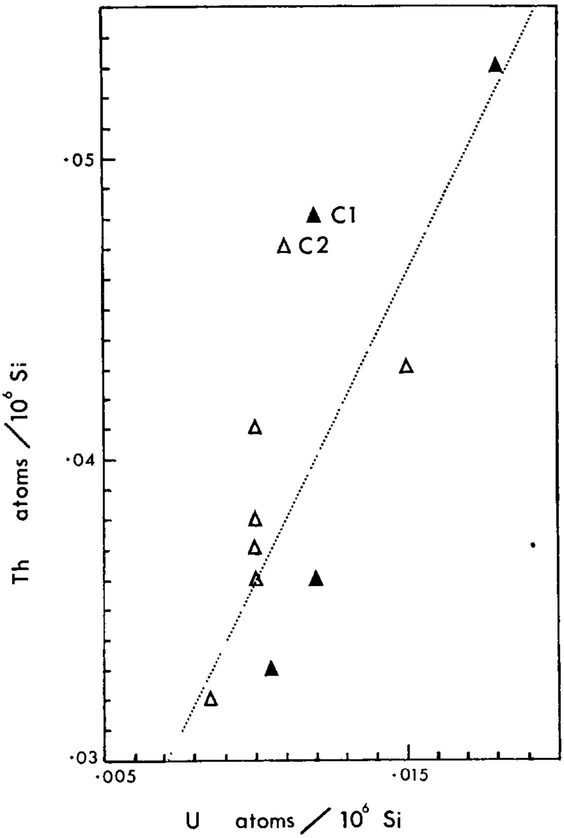

FIG. 3.—Thorium and uranium atomic abundances relative to 10^6 Si atoms for C1 and C2 group chondrites.

that for both uranium and thorium significant differences exist. Because of the uniformity within the other chemical groups and the similarity of the C1, C2 and C4 groups the discrepancy in the case of the C3 group is rather surprising. It should be remembered that the control on the sampling of Bencubbin, Lancé and Warrenton was not good. None of the samples were prepared specially for the present study, and there would have been strong grounds for rejection on the basis of the high abundances found, had it not been for the previously published high uranium measurement on Lancé.[22] This value was even higher than those found in our work. On the other hand a later,[23] though probably less reliable, uranium analysis of Lancé gave a result which was only one quarter of the earlier published value. It is clear that more uranium and thorium analyses of the C3 group, under closely controlled conditions, are necessary to confirm or refute the results for this group obtained in the present study. For this reason the cosmochemical implication of the C3 abundances will not be discussed further.

Within the C1 group, the variations of the uranium and thorium abundances are correlated. If each fall is given unit weight, the correlation coefficient (r) is 0·80. Within the C2 group, the two elements are also correlated, r being 0·71 for the weighted atomic abundances. A test of the slopes of the regression lines fitted to the C1 and C2 group chondrites showed no significant difference in slope, therefore, the two groups were pooled. The correlation coefficient for the pooled values is 0·80. The regression line fitted to the pooled C1 and C2 abundances is shown in Fig. 3.

CONCLUSIONS

If the analyses for uranium and thorium made in the present study are considered in the light of the Van Schmus–Wood chondrite classification, the following conclusions can be drawn.

1. With the possible exception of the C3 group, the mean abundances for each petrologic type within a particular chemical group are very similar.
2. The mean abundances of the three chemical groups which make up the ordinary chondrites (*i.e.*, H, L and LL) are identical.
3. The mean uranium and thorium abundances of the chemical groups decrease in the order C > (H, L, LL) > E.
4. In view of the apparently anomalous abundances (especially for thorium) found in the C3 group, more analyses of carefully selected and prepared samples are required to establish firmly the abundances in this group.

Acknowledgements—We thank the many donors of chondrite samples (see Appendix A) for their generosity. This work was supported in part by a grant from the Australian Institute of Nuclear Science and Engineering.

Zusammenfassung—Für 42 "Fälle" von Chondrit-Meteoriten und einen "Fund", die 15 der 20 Chondrit-Typen nach van Schmus und Wood einschließen, werden Neutronenaktivierungsanalysen auf Uran und Thorium mitgeteilt. Der mittlere Uran- und Thoriumgehalt der 5 chemischen Gruppen zeigt einen Gang: C-Gruppe ($U = 0{,}012_0$ Atome/10^6 Si-Atome, $Th = 0{,}045_4$ Atome/10^6 Si-Atome, $Th/U = 3{,}7_8$) > H-, L- und LL-Gruppe ($U = 0{,}008_3$, $Th = 0{,}028_0$, $Th/U = 3{,}4_5$) > E-Gruppe ($U = 0{,}005_9$, $Th = 0{,}021_8$, $Th/U = 3{,}6_9$). Vielleicht mit Ausnahme der C3-Chondrite sind die mittleren Gehalte jedes petrologischen Typs innerhalb einer chemischen Gruppe dieselben.

Résumé—On rapporte les analyses par activation de neutrons pour l'uranium et le thorium pour 42 météorites type chondrite "chute" et 1 "trouvée" couvrant 15 des 20 types de chondrite Van Schmus–Wood. Les abondances moyennes en uranium et thorium des 5 groupes chimiques montrent une tendance suivante avec le groupe C (U = $0{,}012_0$ atomes/10^6 atomes Si, Th = $0{,}045_4$ atomes/10^6 atomes Si, Th/U = $3{,}7_8$ > groupes H, L et LL (U = $0{,}008_3$, Th = $0{,}028_0$, Th/U = $3{,}4_8$ > groupe E (U = $0{,}005_9$, Th = $0{,}021_8$, Th/U = $3{,}6_9$. Avec l'exception possible des chondrites C3, les abondances moyennes pour chaque type pétrologique à l'intérieur d'un groupe chimique donné sont identiques.

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APPENDIX A.—SOURCES OF METEORITE SPECIMENS

	Class	Source	Preparation
Abee	E4	A	c
Alais	C1	B	a
Allegan	H5	C	a
Bandong	LL6	D	a
Beardsley	H5	D	a
Benares	LL6	D	a
Bencubbin*	C3	E	b
"Bialystok"†	LL6	D	b
Bjurbole	L4	C	a
Chainpur	LL3	D	a
Cold Bokkeveld	C2	D	a
Farmington I	L5	C	b
Farmington II	L5	D	a
Forest Vale I	H4	D	b
Forest Vale II	H4	D	a
Holbrook	L6	C	a
Homestead I	L5	C	b
Homestead II	L5	C	a
Hvittis	E6	D	b
Indarch	E4		
Ivuna I	C1	A	c
Ivuna II	C1	F	a
Ivuna III	C1	G	a
Karoonda	C4	H	b
Khairpur I	E6	G	b
Khairpur II	E6	D	a
Khohar	L3	D	a
Knyahinya	L5	D	a
Lancé	C3	D	b
Mighei	C2	D	a
Mocs	L6	C	b
Mokoia	C2	I	b
Mount Browne I	H6	C	b
Mount Browne II	H6	C	a
Murray	C2	J	a
Nawapali	C2	K	a
Ngawi	L3	D	a
Ochansk	H4	D	a
Orgueil IA	C1	D	b
Orgueil IB	C1	D	a
Orgueil II	C1	L	c
Orgueil III	C1	D	a
Orgueil IV	C1	A	a
Perpeti	L6	D	b

APPENDIX A. (*Contd.*)

	Class	Source	Preparation
Pillistfer	E6	D	a
Pultusk	H5	D	a
Renazzo I	C2	G	a
Renazzo II	C2	J	a
Renazzo III	C2	M	a
Richardton	H5	D	a
St. Mark's I	E5	G	b
St. Mark's II	E5	J	a
St. Mark's III	E5	N	a
St. Michel	L6	D	a
Staroe Boriskino	C2	O	a
Tonk	C1	K	a
Warrenton	C3	C	b
Zhovtnevyi I	H6	C	b
Zhovtnevyi II	H6	C	a

* The Bencubbin sample analysed was a small C3 inclusion from this unique mixed meteorite.

† Bialystok is generally considered to be a howardite; however, our sample bearing that name is undoubtedly an amphoterite and has been tentatively put in the LL6 group.

Source code

A	Dr. L. P. Greenland, U.S. Geological Survey, Washington D.C.
B	Prof. J. Orcel, Natural History Museum, Paris.
C	Mr. R. O. Chalmers, Australian Museum, Sydney, N.S.W.
D	Kyancutta Museum, South Australia.
E	Dr. R. D. L. Pride, West Australia Museum, Perth, W.A.
F	The Commissioner, Mineral Resources Division, Tanzania.
G	Dr. B. Mason, American Museum of Natural History, New York.
H	South Australian Museum, Adelaide, S.A.
I	Mr. J. G. Smart, Wanganui Public Museum, Wanganui, New Zealand.
J	Dr. E. P. Henderson, U.S. Natural History Museum, Washington D.C.
K	Dr. M. V. N. Murthy, Geological Survey of India, Calcutta.
L	Prof. W. D. Ehmann, University of Kentucky, Lexington.
M	Prof. P. Gallitelli, University of Bologna, Italy.
N	South African Museum, Cape Town, South Africa.
O	Dr. E. L. Krinov, Committee on Meteorites, U.S.S.R. Academy of Sciences, Moscow.

Preparation code

a	Prepared by us especially for the present work.
b	Prepared in this department, but not by us, nor specially for this work.
c	Sample received as a powder and used without further treatment.

APPENDIX B.—URANIUM AND THORIUM IN CHONDRITES REJECTED AS PROBABLY CONTAMINATED

Sample	Group	Uranium, $\mu g/g$	Thorium, $\mu g/g$	Reason for rejection
Bjurbole	L4	$\left.\begin{array}{r}24{\cdot}1 \pm 0{\cdot}5\\ 24{\cdot}2 \pm 0{\cdot}6\end{array}\right\}$ 24·2	$\left.\begin{array}{r}84{\cdot}9 \pm 1{\cdot}1\\ 79{\cdot}4 \pm 1{\cdot}0\end{array}\right\}$ 82·1	1, 6
Farmington I	L5	$\left.\begin{array}{r}98{\cdot}2 \pm 1{\cdot}6\\ 86{\cdot}7 \pm 1{\cdot}2\end{array}\right\}$ 92·4	$\left.\begin{array}{r}80{\cdot}2 \pm 1{\cdot}2\\ 129{\cdot}2 \pm 1{\cdot}8\end{array}\right\}$ 105	1, 2, 3, 5
Forest Vale I	H4	$\left.\begin{array}{r}32{\cdot}3 \pm 0{\cdot}8\\ 31{\cdot}5 \pm 0{\cdot}6\end{array}\right\}$ 31·9	$\left.\begin{array}{r}44{\cdot}8 \pm 0{\cdot}9\\ 50{\cdot}0 \pm 0{\cdot}7\end{array}\right\}$ 47·4	1, 3, 5

APPENDIX B. (*Contd.*)

Sample	Group	Uranium, $\mu g/g$	Thorium, $\mu g/g$	Reason for rejection
Homestead I	L5	66·4 ± 1·0 150 ± 2	45·9 ± 0·5 47·3 ± 0·6 } 46·6	1, 2, 3, 5
Khairpur I	E6	647 ± 9 590 ± 8 } 619	439 ± 6 418 ± 8 } 429	1, 3, 5
Mount Browne I	H6	240 ± 4 42·6 ± 0·7	40·5 ± 0·6 39·2 ± 0·5 } 39·9	1, 2, 3, 5
Mocs	L6	73·6 ± 2·5 93·3 ± 1·9 } 83·5	52·0 ± 2·8 58·1 ± 1·6 } 55·1	1, 3
Orgueil III	C1	12·9 ± 0·3 17·4 ± 0·5 } 15·2	44·4 ± 1·8 99·1 ± 4·0	2, 4, 6
Renazzo I	C2	626 ± 10 826 ± 21 } 726	55·5 ± 1·1 69·1 ± 1·0 } 62·3	1, 4, 5
St. Mark's I	E5	3,290 ± 40 3,050 ± 50 } 3,170	1,350 ± 20 1,210 ± 10 } 1,280	1, 3, 5
Zhovtnevyi 1	H6	29·6 ± 0·6 35·6 ± 0·7 } 32·6	41·5 ± 0·4 42·1 ± 0·5 } 41·8	1, 3, 5

Rejection code

1. Higher than previously published values for the same fall or for similar meteorites.
2. Internally inconsistent showing both wide differences between duplicates and variable Th/U ratios.
3. Sample not a powder specially prepared for this work.
4. Sample prepared from small sample making rigorous decontamination impossible.
5. Repeat analyses on carefully prepared sample do not agree with rejected results.
6. See discussion in text.

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NEUTRON-ACTIVATION ANALYSIS FOR THE STUDY OF METALLOGENIC PROVINCES

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Summary—The application of instrumental neutron-activation analysis to the study of metallogenic provinces is outlined. Iron, scandium and lanthanum are measured in uncrushed, whole-rock specimens, and the results indicate trace element compositional trends over the 50-mile traverse studied. These trends extend through a number of different formations and rock types, and reflect structural features mapped by others using conventional techniques.

METALLOGENY is concerned with the study of the deposition and distribution of minerals and ores during the evolution of the earth's crust. The extremely diverse nature of the earth's crust disqualifies attempts to draw valid inferences from a small number of isolated samples, and geologists who are interested in plotting the occurrence of various elements usually overcome this limitation by confining themselves to the choice and comparison of similar or identical rock types.

It is customary to isolate the minerals in rocks under study, and to subject these minerals to various forms of chemical analysis. If the results obtained are disappointing—as was the case with the analyses of the standard G-1 and W-1 samples, where over 100 reputable laboratories in 22 countries quoted different analytical results[1]—the analyst may either be utilizing a chemical method that is lacking in accuracy or precision, or the sampling technique may be statistically invalid. Elemental contamination may also have occurred during sample crushing and preparation, or other errors may have invalidated the results.

Metallogenesis adopts the approach that attention has to be focused on whole regions, termed "metallogenic provinces and epochs", rather than on individual sampling sites. Bilibin[2] made a fundamental study of some regions of the ore deposits of the U.S.S.R. He classified the ore deposits on the basis of the stage of mobile belt development. Bilibin recognized that the concentration of groups of elements in the ore is basically determined by the presence of superimposed structures in the metallogenic regions of the belt. Petrascheck[3] defines a metallogenic province as "the entity of mineral deposits that formed during a tectonic-metallogenic epoch within a major tectonic unit, and which are characterized by related mineral composition, form of the deposits and intensity of mineralization."

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* On assignment from the South African National Institute for Metallurgy, Johannesburg.

† On assignment from the Philippine Atomic Energy Commission, Manila; NAS-IAEA Fellow.

Scope of metallogenic studies

In recent years the concept of metallogenesis has enjoyed strong support from Russian geologists,[4] who are searching for new mineral sources. They appear to be convinced that metallogeny of large areas holds promise for identifying areas attractive for further exploration of certain trends into smaller unmapped and inaccessible areas.

A study of both the minor and trace elements is of interest, since their distribution depends largely on the presence of concentrating host minerals. Rodionov,[5] in his studies of igneous rocks, noted that elements which are dispersed among the minerals of a rock have essentially normal distribution. Elements that tend to concentrate in one particular mineral tend to display a log normal distribution. A fundamental principle apparently being followed is that most trace elements are present in extremely low concentrations, and consequently display a rather different distribution in comparison to that of the major elements which form the minerals of the rocks.[6]

It is to be expected that most metallic trace elements will remain generally within their original regional limits, in spite of superimposed geological processes occurring within the region. Geological changes will probably maximize or minimize the trace elemental concentration in specific locations. A study of the overall pattern or trends of trace and minor element metallogenic provinces should, therefore, be of interest for geochemical mapping purposes, and for purposes of economic geology.

An example would be the comparison of ore metals from the Soviet Union with Brazilian granites. Bilibin[2] summarizes the distribution between different stages of mobile belt development of elements in ore deposits of the U.S.S.R. by the triangle shown in Fig. 1. Herz and Dutra[7] on the other hand analysed spectrographically 39 granite samples from the Brazilian shield, covering different age groups. The main abundances of the trace elements in whole-rock samples are grouped under the corresponding age groups in Fig. 1. The broad agreements with Bilibin's findings are striking, except for lead, which could equally well have been grouped with molybdenum and beryllium. Similarly, scandium and gallium show insignificant differences for the various age groups, suggesting similar trace elemental relationships in both continents.

Further support for the metallogenic approach, although in this case confined to the analyses of minerals, comes from Burnham.[8] He showed that the trace element concentration of sulphides in the south-western United States and northern Mexico could be contoured. He determined silver, bismuth, cadmium, cobalt, gallium, manganese, molybdenum, nickel, tin, indium, thallium and antimony in chalcopyrites and sphalerites obtained from ore deposits covering an area 2000 miles long. Burnham showed that variations of the trace element content were generally small compared to variations between regions.

Rose[9] carried Burnham's investigation further and concluded that on a regional basis, both areas under consideration, *i.e.*, Central district (New Mexico) and Bingham district (Utah), showed groupings defined by geographic location, trace element content, and geological structure. Also, on a regional scale, lateral and vertical zoning appeared to exist and some variations appeared to correlate with rock type.

An interesting potential application of metallogenesis would be in the study of the continental-drift theory.[10] Schuiling[11] chose the element tin, since it shows a strongly inhomogeneous distribution. A plot of all the known economic and uneconomic occurrences of this element on Bullard's combined continents,[12] yielded "tin belts" across the Americas, Africa, and Europe, as shown in Fig. 2. These data not only render support for the continental-drift theory, but also provide useful information for prospectors and support Bilibin's theory. Schuiling used over 500 references, but emphasized that these belts have no hard and fast boundaries. The tin belts may be

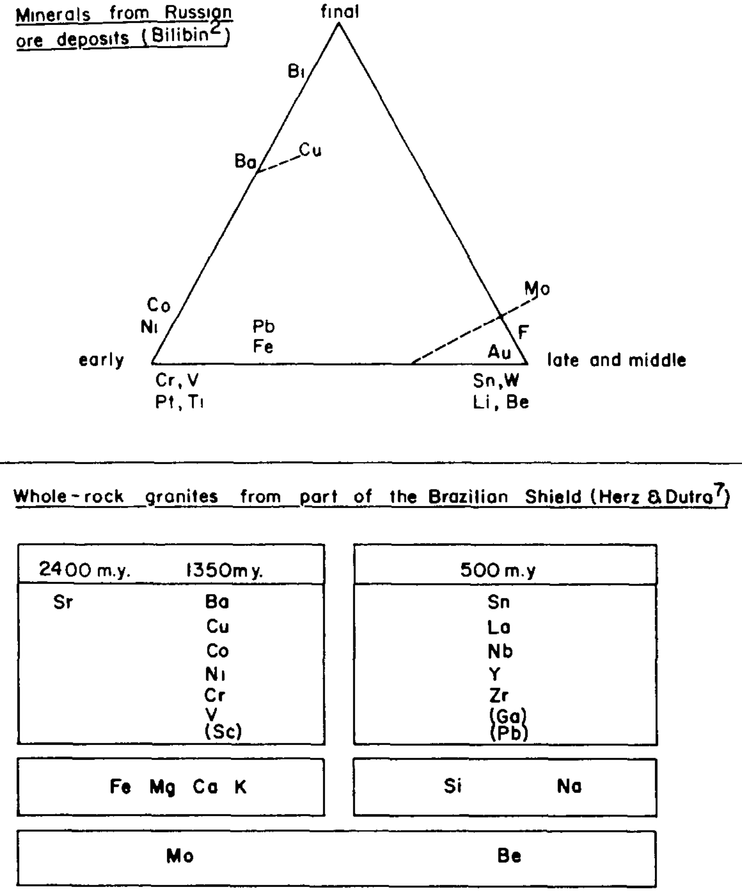

Fig. 1.—Distribution of trace and minor elements during various stages of mobile belt development.

correlated to the rough outline of tin "endogenous" mineralization across the continents.

The study of metallogenic provinces by nuclear-activation analysis

If the principles and evidence for metallogenic provinces are accepted, the desirability of an extensive study of multi-element compositional ratios as obtained by large scale nuclear-activation analysis methods suggests itself. Some of the potential advantages which may be gained may be summarized as follows.

(*a*) The automated neutron-activation analysis system at Texas A & M[13,14] is sufficiently rapid for large numbers of rock samples to be analysed in a relatively short period of time. A large number of determinations is required to validate statistically the metallogenic mapping approach.

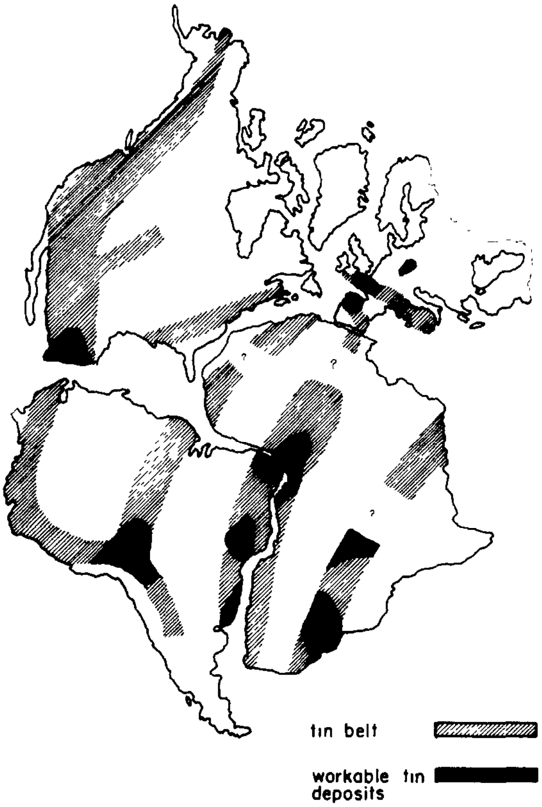

FIG. 2.—Tin belts across "Pangeae", by R. D. Schuiling.[11]

(*b*) The technique of reactor-activation analysis results in a variety of elements becoming activated. Multi-elemental ratios may therefore also be derived to serve as characteristics to establish the similarity of groups of samples and their elemental trends. The latter approach may help to explain some anomalies encountered in rock dating, where usually two elements or isotopes of one element are compared.

(*c*) The inevitable large volume of data can conveniently be stored, compared and retrieved by a computer. Yule's "Hevesy" program[15] locates the gamma-ray energy peaks, calculates the photo-peak area from smoothed data, and gives the elemental concentration relative to a reference standard, after correcting for the decay time.

(*d*) The limits of detection of many elements are more favourable for reactor neutron-activation analysis than for other techniques.[16] Certain trace elements also have reasonably good cross-sections for 14-MeV neutron activation, but the work described below is limited to reactor activation products.

(*e*) If large numbers of samples have to be handled, their preparation and manipulation becomes a major problem, which will be significantly reduced if whole-rock specimens can be subjected to activation analyses with reasonable results, as described below.

(*f*) The many variables appertaining to activation analysis, such as variety of nuclear reactions, different half-lives, cross-sections, thresholds and abundances afford the analyst the opportunity to choose the best conditions for a variety of determinations. Once the specimen has been activated, the resulting spectrum may be measured repeatedly to yield additional information on various constituents.

(*g*) Nuclear-activation analysis is isotopically specific and total oxygen, for example, may be determined directly, irrespective of its elemental combination. Alternatively, different reactions permit determination of certain isotopes, such as oxygen-16 and oxygen-18, for example, in addition to total oxygen.

The various methods of activation analysis should therefore prove to be useful for the study of metallogenic provinces, for geological mapping purposes, for prospecting, or for such studies as the continental-drift theory.

EXPERIMENTAL

In order to determine the feasibility of this approach it was decided to test an area which has been extensively studied by others. Samples were taken along a diametric traverse, which passes through and extends beyond the Enchanted Rock batholith near Llano, Texas. By analysing samples from 20 sites extending over a distance of approximately 50 miles, it was hoped that regional trends would be indicated by certain trace elements. Their distribution, and concentration relative to the standard rock, irrespective of host rock types, could then be interpreted in relation to a metallogenic province.

The area chosen is not associated with any economic mineral deposit, but sufficient geological[17] and analytical[17-20] data are available to indicate that a variety of rock types is easily accessible. Adjacent to the batholith, sedimentary and metamorphic rocks occur. The pluton itself is about 10 miles across and the four concentric zones shown in Fig. 3, consist[17] of (*a*) the outer zone—medium to coarse leucogranite and granite; (*b*) the intermediate zone—medium to coarse granite and quartz monzonite; (*c*) the intermediate central zone—coarse quartz monzonite and alkalic grandiorite; (*d*) the core—fine to medium leuco-quartz monzonite and leucogranite.

Collection of samples

Ten 30-lb fresh granite samples were taken from the surface of the batholith itself at positions 1–10, as indicated in Fig. 3. Three chips weighing approximately 1 g each were broken off at opposite ends of each sample and placed in clean polyethylene vials.

Four sedimentary samples were taken at random, south-west of the batholith along Farm Road 2323, at distances indicated in Table I. A further 5 samples were taken north-east of the batholith along the same road towards Lake Buchanan. Details of the different rock types samples are given in Table I.

Analysis of whole-rock specimens

The whole-rock samples were weighed and without further preparation were irradiated for 2 hr in the Texas A & M Research Reactor at a thermal neutron flux of approximately 2×10^{12} n. cm^{-2}. sec^{-1}. Samples of the standard granite rock G-2 were also included to serve as reference standards.

The samples were all counted about 14 days after the end of irradiation. A 19-cm^3 lithium-drifted germanium detector was used in conjunction with a Victoreen 3200-channel analyser. In Figs. 4, 5 and 6 some of the observed spectra are shown, measured over a counting period of 60 min analyser live-time.

The photopeak areas at 0·889, 1·596 and 1·10 MeV were calculated by an adapted version of Covell's method[21] to yield quantitative values for scandium-46, lanthanum-140 and iron-59 respectively. The natural activity as determined by counting the unirradiated samples was found to be too low to

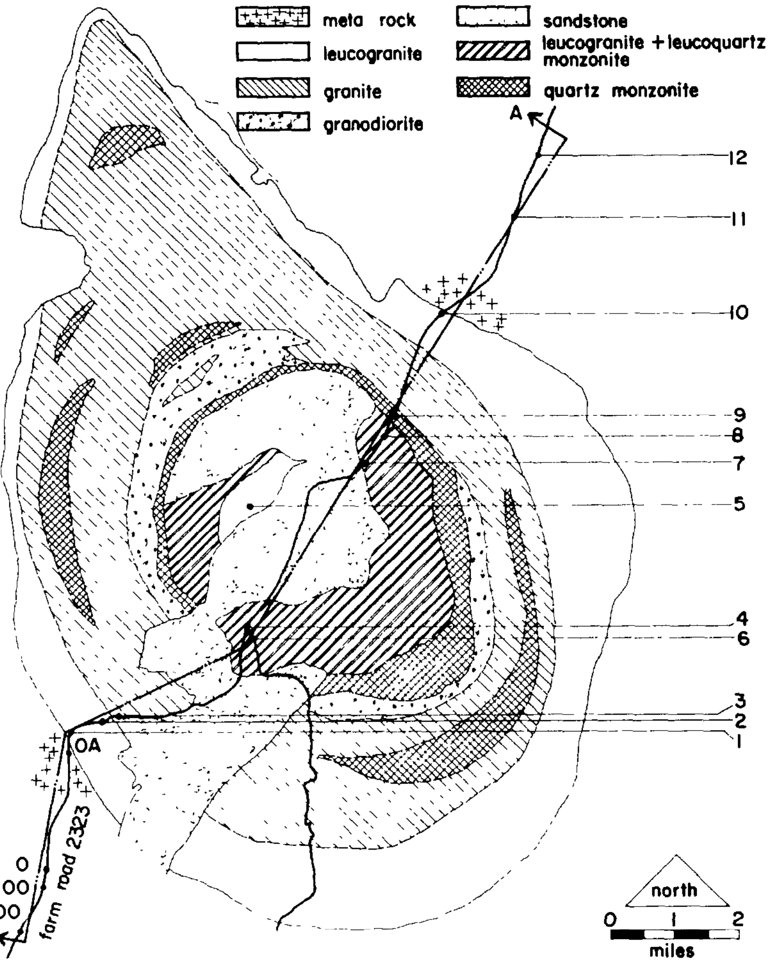

Fig. 3.—Sampling sites along a diametric traverse of the Llano Enchanted Rock batholith, Texas (after Hutchinson[17]).

contribute significantly. No gamma-ray emitters were found that interfered with the lanthanum-140 1·600-MeV gamma-ray.

A study of elemental standards[15] revealed that the scandium-46 gamma-ray at 0·889 MeV is of higher activity and also completely resolved from the Compton edge of its 1·119-MeV gamma-ray counterpart. It was found that for the range of concentrations encountered, the 0·869-MeV gamma-ray of lanthanum-140 contributed less than 1% to the 0·889-MeV gamma-ray of scandium-46.

The values for iron-59, as determined from the 1·100-MeV gamma-ray peak may be somewhat less accurate, since both the lanthanum-140 1·087-MeV and the europium-152 1·110-MeV gamma-rays interfere. The over-all interferences, however, are less than 2% of the measured activity of iron-59, for the concentrations encountered in the Llano Enchanted Rock batholith.[17,19] After correction for neutron-flux variations and normalization to a sample weight of 1 g and a decay time of 14 days, the values given in Table I were obtained. The concentrations are expressed relative to the values obtained by Gordon *et al.*[22] for the standard granite rock sample G-2, (3·5 ppm Sc = 21934 counts/hr/g; 81·0 ppm La = 4701 counts/hr/g; 1·72% Fe = 1778 counts/hr/g).

TABLE I.—ANALYTICAL RESULTS FOR UNCRUSHED LLANO SAMPLES

No.	Sample		Scandium	Lanthanum	Iron
	Distance from centre of pluton, *miles*	Rock-type	*ppm*	*ppm*	%
000	10 SW	Shale	3·4 ± 0·3*	11·9 ± 0·3*	0·28 ± 0·02*
00	6 SW	Limestone	1·4 ± 0·3	4·3 ± 0·1	0·25 ± 0·02
0	5¼ SW	Meta sediment	1·6 ± 0·3	10·9 ± 0·3	0·63 ± 0·02
0A	5 SW	Meta sediment	2·6 ± 0·3	18·7 ± 0·5	0·82 ± 0·03
1	5 SW	Leucogranite	0·8 ± 0·1	31·8 ± 0·6	1·72 ± 0·06
			1·2 ± 0·2	36·5 ± 0·7	1·45 ± 0·06
			1·4 ± 0·3	31·4 ± 0·6	1·19 ± 0·05
2	4½ SW	Leucogranite	2·4 ± 0·3	23·8 ± 0·5	1·76 ± 0·06
			2·8 ± 0·3	29·2 ± 0·6	2·16 ± 0·07
			3·3 ± 0·3	27·2 ± 0·6	2·00 ± 0·07
3	4¼ SW	Granite	7·0 ± 0·3	58·8 ± 0·8	2·44 ± 0·07
			0·7 ± 0·1	23·0 ± 0·5	2·14 ± 0·07
			3·6 ± 0·3	56·2 ± 0·8	2·49 ± 0·07
4	2 SW	Leucoquartz Monzonite	5·2 ± 0·3	37·9 ± 0·7	3·23 ± 0·08
			3·7 ± 0·3	23·0 ± 0·5	3·45 ± 0·08
			4·6 ± 0·3	33·4 ± 0·6	3·09 ± 0·08
6	2 SW	Leucoquartz Monzonite	3·9 ± 0·3	16·9 ± 0·5	2·61 ± 0·07
			5·2 ± 0·3	20·6 ± 0·5	2·87 ± 0·07
			4·4 ± 0·3	17·3 ± 0·5	2·88 ± 0·07
5	0	Leucogranite	3·0 ± 0·3	20·4 ± 0·5	2·54 ± 0·07
			3·3 ± 0·3	27·6 ± 0·6	2·59 ± 0·07
			3·3 ± 0·3	26·1 ± 0·6	2·24 ± 0·07
7	2 NE	Leucoquartz Monzonite	4·1 ± 0·3	46·4 ± 0·7	2·88 ± 0·07
			4·6 ± 0·3	56·3 ± 0·9	3·12 ± 0·08
			4·7 ± 0·3	50·0 ± 0·8	2·75 ± 0·07
8	3 NE	Leucoquartz Monzonite	4·0 ± 0·3	31·1 ± 0·6	2·37 ± 0·07
			4·0 ± 0·3	38·9 ± 0·7	2·24 ± 0·07
			4·0 ± 0·3	33·2 ± 0·6	2·62 ± 0·07
9	3½ NE	Quartz Monzonite	3·2 ± 0·3	51·7 ± 0·8	2·67 ± 0·07
			3·1 ± 0·3	50·3 ± 0·8	2·64 ± 0·07
			3·8 ± 0·3	51·0 ± 0·8	2·94 ± 0·07
10	5 NE	Leucogranite	2·1 ± 0·3	88·8 ± 2·0	1·48 ± 0·06
			2·3 ± 0·3	100·3 ± 2·5	2·08 ± 0·07
			2·4 ± 0·3	78·1 ± 1·6	1·81 ± 0·06
11	7 NE	Leucogranite	2·3 ± 0·3	39·6 ± 0·7	3·10 ± 0·08
12	8 NE	Leucogranite	3·3 ± 0·3	50·5 ± 0·8	3·89 ± 0·09
13	13 NE	Granite	1·2 ± 0·2	45·7 ± 0·7	2·21 ± 0·07
14	14 NE	Leucoquartz Monzonite	2·0 ± 0·3	23·0 ± 0·6	2·47 ± 0·07
15	37 NE	Orthoclase-Biotite Hornfels	8·1 ± 0·4	25·3 ± 0·6	3·56 ± 0·08

* Error quoted is standard deviation calculated as square root of mean count.

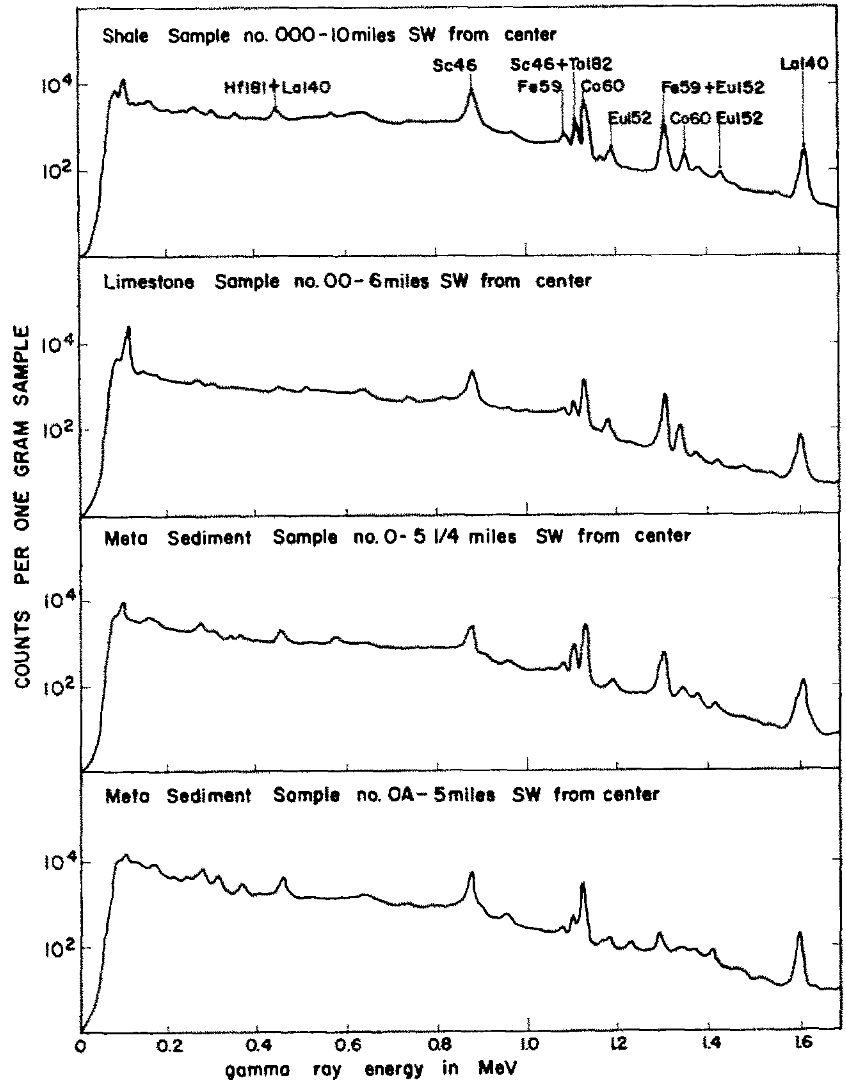

FIG. 4.—Comparison of spectra from different rock types SW of the Llano Enchanted Rock batholith.

DISCUSSION

From Table I it can be concluded that the precision of the analytical results obtained from whole-rock specimens is not very good. In geological mapping the relative values are, however, more informative than the absolute concentrations and in Fig. 7 the elemental trends of a portion of a metallogenic province are indicated. Iron, scandium and lanthanum all follow a compositional trend beyond the pluton boundary irrespective of the host-rock type. The sedimentary rocks may therefore be considered to be probable erosional derivatives of the batholith. Hutchinson[17] and Ragland *et al.*[19] also consider the inner core of the batholith to be a separate later

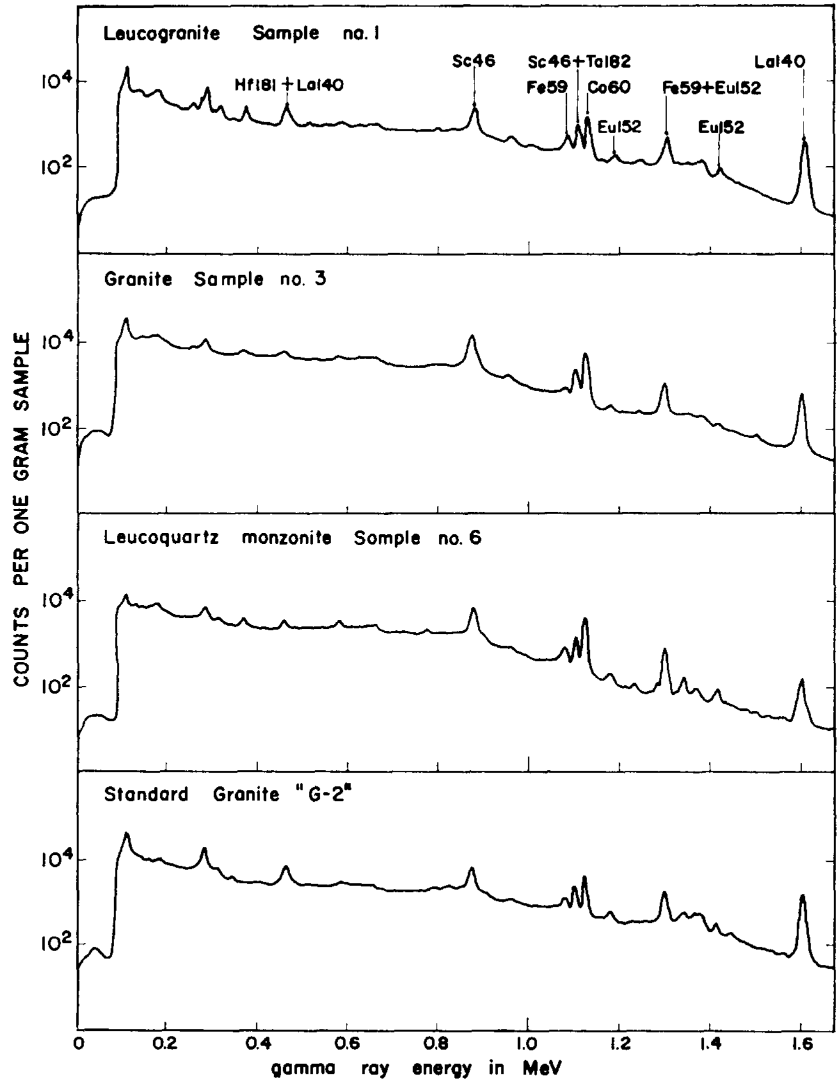

Fig. 5.—Comparison of spectra from G-2 and granitic rocks within the Llano Enchanted Rock batholith.

intrusive, since the average composition of this relatively fine-grained zone falls off rather abruptly.

Both scandium and iron appear to become progressively more concentrated towards the centre of the batholith. This trend may be classified as a variation within a specific rock type. The granitic rocks involved are genetically related and the compositional trends of scandium and iron appear to be due to the fractional differentiation of a common parent magma. The symmetry of the trends shown in Fig. 7 is in agreement with the generally accepted and mapped[19–20] nearly concentric zonal arrangement of the granitic rock types shown in Fig. 3.

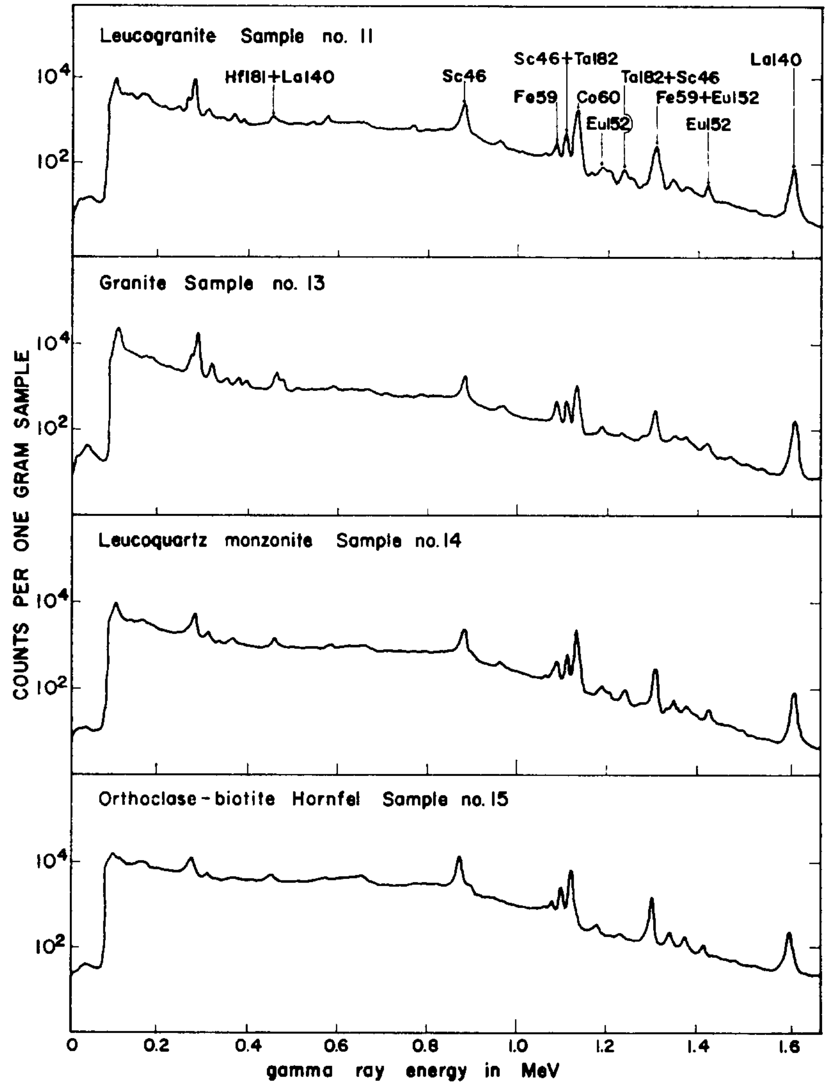

Fig. 6.—Comparison of spectra from different rock types NE of the Llano Enchanted Rock batholith.

There is also evidence that the core is a later intrusive,[17,19] since the undulation at the centre of the core suggests a dilution of scandium and iron due to the introduction of materials poor in these elements. The relatively high scandium content of the hornfels sample (No. 15 in Table I) probably reflects the tendency for biotites to concentrate scandium.

Lanthanum on the other hand appears to be fairly uniformly distributed over most of the samples of granitic rocks of the batholith. Towards the north-eastern boundary, however, the lanthanum content rises appreciably, as shown in Fig. 7. Beyond the north-east outer zone lanthanum appears again to follow a more uniform

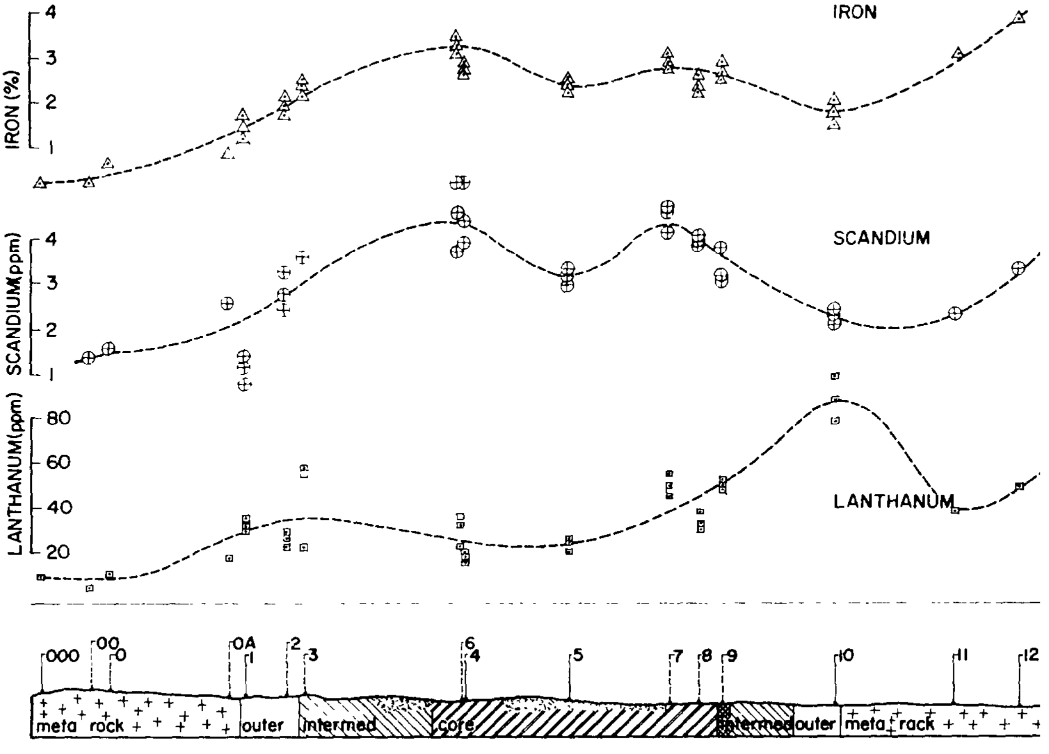

FIG. 7.—Distribution of iron, scandium and lanthanum along the SW-NE diametric traverse of the Llano Enchanted Rock batholith, Texas (Section A-A′ of Fig. 3).

pattern of distribution, as shown in Table I. A possible explanation could be that marked metamorphism occurred in the north-east outer zone of the batholith, although Billings *et al.*[18] found no evidence for regional metasomatism.

CONCLUSIONS

Although this investigation was limited to the study of a very small part of a possible metallogenic province, the following deductions may be made.

(*i*) Activation analysis is indeed capable of providing useful data which may help to substantiate the concept of "metallogenic provinces." The advantages outlined above contribute to the desirability of using this technique for purposes of extensive geological mapping of both economic and uneconomic regions.

(*ii*) All three elements considered displayed a certain amount of continuity irrespective of the host-rock type. Iron, scandium and lanthanum were chosen at random, but we have reason to believe that other trace and minor constituents also display similar trends or similarities.

(*iii*) Both compositional trends and similarities should prove beneficial for large scale mineral exploration purposes of inaccessible and relatively unmapped regions. Putman and Burnham[23] claim that a concentration mechanism such as a superimposed geological process or processes, operating in a magmatic body with a relatively high initial metal content, has a proportionally better chance of producing an ore deposit.

(*iv*) A decay time of 14 days had to be allowed for the bulk of the sodium activity to disappear. Iron, scandium and lanthanum could then be determined with sufficient accuracy, on whole-rock specimens, to indicate compositional trends as shown in Fig. 7. Experiments are, however, currently under way to compare the precision of the method with that obtainable from samples subjected to crushing and subsequent mixing.

(*v*) After approximately 40 days[10] some of the longer-lived isotopes will be determinable. Useful elemental ratios may then be obtained that will give information on elemental mobility, behaviour and inter-relationships.

(*vi*) It would be interesting to extend this investigation to other plutons of similar as well as different origins. Areas of known economic interest should also be studied and the crucial test of the method would be to see whether extrapolations of results do indeed predict regions of interest.

Acknowledgements—The authors are grateful for the assistance rendered by members of the Geology Department of Texas A & M University, and valuable discussions with Dr. Tom Tieh and Hans Swolfs in particular. The assistance of Dr. H. P. Yule and Dr. L. E. Fite, both of the Activation Analysis Research Laboratory, is sincerely appreciated.

Zusammenfassung—Die Anwendung der instrumentellen Neutronenaktivierungsanalyse auf die Untersuchung metallführender Bezirke wird skizziert. Eisen, Scandium und Lanthan werden in nicht zerkleinerten Proben aus unversehrtem Gestein gemessen; die Ergebnisse weisen auf systematische Variationen der Zusammensetzung in dem 50 Meilen langen Aufschluß hin. Diese systematischen Abhängigkeiten erstrecken sich über eine Anzahl verschiedener Gesteinsformationen und -typen und spiegeln strukturelle Eigentümlichkeiten wider, die von anderen Autoren mit konventionellen Verfahren kartiert wurden.

Résumé—On donne un aperçu de l'application de l'analyse instrumentale par activation de neutrons à l'étude de terrains métallogènes. On mesure le fer, le scandium et le lanthane dans des spécimens de roches entières, non broyés, et les résultats montrent les tendances de composition en élément à l'état de traces sur le parcours de 50 miles étudié. Ces tendances se développent à travers un certain nombre de formations et de types de roches différents et réflètent les caractères structuraux établis par d'autres en utilisant des techniques ordinaires.

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DETERMINATION OF HAFNIUM BY NEUTRON ACTIVATION, AND VARIATION IN THE Zr/Hf RATIO OF SOME GRANITE MASSES

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Summary—A fairly quick method for the separation of hafnium from irradiated rock samples is described and results of the hafnium determinations are reported. The distribution of zirconium and hafnium and the variation of the Zr/Hf ratio in three calc-alkali granite masses are discussed. Reasons are suggested for the observed decrease in the Zr/Hf ratio during the crystallization of igneous rocks.

SEVERAL authors have described the neutron-activation determination of hafnium in rocks and meteorites.[1–4] The separation described by Merz[1] and by Merz and Schrager[3] does not remove protactinium–233 [produced by the reaction $^{232}\mathrm{Th}(n, \gamma)$ $^{233}\mathrm{Th} \xrightarrow{\beta} {}^{233}\mathrm{Pa}$] from zirconium and hafnium, a step necessary in the present work because the bulk of the activity measurements had to be made with a single-channel γ-ray spectrometer. The procedure described is a fairly fast method of separating zirconium and hafnium from irradiated rock samples and, under the irradiation and cooling conditions used, it was unnecessary to separate zirconium from hafnium. The same results were obtained when either zirconium or hafnium was used as carrier, so the separation described seems to cause no fractionation of zirconium and hafnium.

EXPERIMENTAL

Reagents

Stock hafnium standard. Dissolve 50 mg of hafnium dioxide in 25 ml of warm concentrated hydrofluoric acid, evaporate to about 5 ml and dilute to 1 l. with water. Store in a polythene bottle.

Working hafnium standard. Dilute an aliquot of the stock solution to produce a solution containing 5–10 μg of Hf/g of solution.

Barium nitrate. Saturated aqueous solution.

Boric acid. Saturated aqueous solution.

Sulphuric acid, 20% (*v*/*v*).

Diammonium hydrogen phosphate. A 10% *w*/*v* aqueous solution and a 2% *w*/*v* solution in 5% *v*/*v* sulphuric acid.

Ammonium nitrate, 5% *w*/*v* aqueous solution.

Ion-exchange columns. Dowex 1 × 8, 100–200 mesh, chloride form. Columns of resin 10 cm long and 1·5 cm in diameter prepared and washed with 10*M* hydrochloric acid before use. Regenerated, after elution of zirconium and hafnium, by treating successively with 60 ml each of 5*M*, 3*M*, 0·5 and 0·01*M* hydrochloric acid and finally conditioned with 30 ml of 10*M* hydrochloric acid.

Irradiation details

Portions (0·1 g) of the working hafnium standard solution and 0·1-g samples of rock powder, sealed in quartz tubes, were irradiated for 3 days at a flux of about 8×10^{12} n.cm^{-2}.sec^{-1} in the core of the reactor at Garching, Munich; 3–4 standards and 8–12 samples were irradiated simultaneously. The irradiated samples and standards were allowed to stand for a week before the separation described below.

Procedure

Samples. 1. Fuse 25 mg of zirconium (or hafnium) dioxide carrier with 0·5 g of sodium peroxide in a nickel crucible. Allow to cool, add irradiated rock sample and 0·5 g each of sodium hydroxide pellets and sodium peroxide. Heat gently to decompose the sample and then raise to red-heat for a further 2–3 min.

2. Place the cooled crucible in a beaker containing 30 ml of water and heat to decompose the cake. Wash the crucible and lid with a little water and heat the contents of the beaker for 5 min to complete the precipitation. Collect the precipitate by centrifuging, discard the liquid and wash once with hot water.

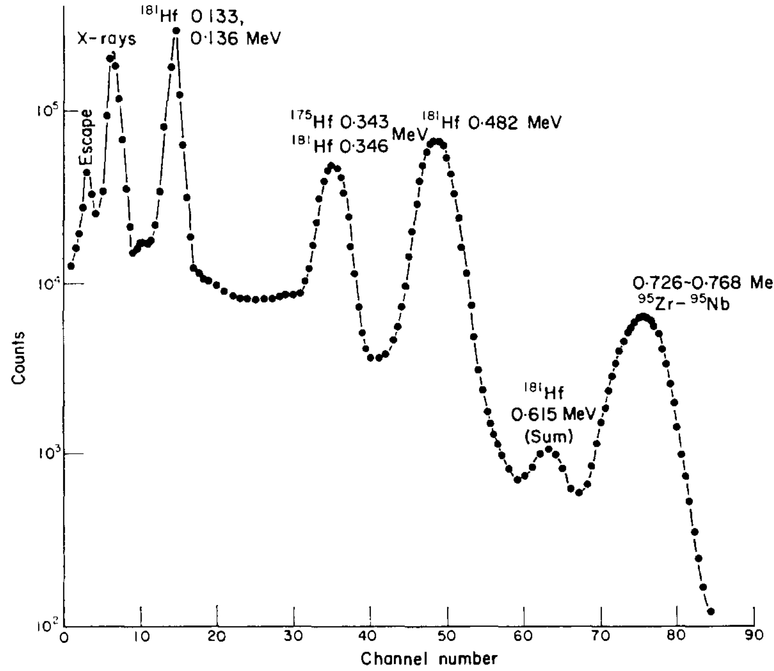

FIG. 1.—The γ-ray spectrum of irradiated ZrO_2, containing 0·5% (*w*/*w*) HfO_2 (Zr/Hf > 100), recorded 1 week after irradiation.

3. Dissolve the precipitate in 20 ml of 10*M* hydrochloric acid, centrifuge and decant the liquid on to the ion-exchange column. Allow the liquid to pass through the column at 2–3 ml/min and then wash the column with 10*M* hydrochloric acid until the effluent is no longer green (due to nickel from the crucible). Elute zirconium and hafnium with 60 ml of 7*M* hydrochloric acid, leaving protactinium-233 on the column.

4. Make the eluate alkaline with concentrated ammonia solution and collect the precipitate by centrifuging.

5. Dissolve the precipitate in 2–3 ml of concentrated hydrofluoric acid, add 2 ml of concentrated nitric acid, 10 ml of water and 10 ml of saturated barium nitrate solution. Mix, allow to stand for 1 min and collect the precipitate of $Ba(Zr, Hf)F_6$ by centrifuging.

6. Dissolve the precipitate in a mixture of 5 ml of water, 2 ml of saturated boric acid and 3 ml of concentrated hydrochloric acid. Dilute to 30 ml with water and add 0·5 ml of concentrated sulphuric acid. Centrifuge and filter to remove barium sulphate.

7. Make the liquid alkaline with concentrated ammonia solution and collect the precipitate by centrifuging.

8. Dissolve the precipitate in 40 ml of 20% *v*/*v* sulphuric acid, add 30 ml of water and 10 ml of 10% *w*/*v* diammonium hydrogen phosphate solution. Mix, heat for 2 hr at 60–80° and collect the precipitate by centrifuging. Wash the precipitate twice with 20 ml of cold 2% *w*/*v* diammonium hydrogen phosphate in 5% *v*/*v* sulphuric acid and then wash with 5% *w*/*v* ammonium nitrate solution until the washings are free from sulphate.

9. Wash the precipitate once with acetone, and transfer it, in the form of a slurry with a little acetone, to a previously ignited (1000°) and weighed porcelain tray. Dry in an oven at 110° and then ignite to constant weight in a furnace starting from cold and rising to 1000° over a period of 1–2 hr. Weigh as ZrP_2O_7 (or HfP_2O_7) to determine the chemical yield.

Standards. 1. Weigh 25 mg of carrier into a teflon dish and dissolve it in 10 ml of hot concentrated hydrofluoric acid. Evaporate to about 5 ml and, using a polythene pipette, add the irradiated standard solution to the carrier. Wash the inside of the quartz capsule first with carrier solution and then with a few ml of 10% *w/v* hydrofluoric acid. Continue washing until all the hafnium activity is removed from the capsule.

2. Add 2 ml of concentrated nitric acid, 10 ml of water and 10 ml of saturated barium nitrate solution, as in stage 5 above. Then proceed with the remainder of stage 5 and stages 6–9.

The chemical yield for samples and standards was usually in the region of 70%.

Activity measurements

The hafnium activity was measured by counting the ^{181}Hf 482-keV γ-ray with a 2 × 2 in. NaI(Tl) detector and a single-channel γ-ray spectrometer. Count-rates were about 2000 cpm for the standards, 200–2000 cpm for the samples and 20–25 cpm for background. Sufficient counts were accumulated to give relative standard deviations in the net count of less than 1% for the standards and less than 2% for the samples. The radiochemical purity of a number of samples was checked by means of a multi-channel γ-ray spectrometer and the only isotopes found were ^{175}Hf, ^{181}Hf and small amounts of ^{95}Zr and ^{95}Nb. The contribution of ^{95}Zr-^{95}Nb to the activity at 482 keV was investigated by irradiating zirconium oxide, carrying out the separation, and comparing the ^{95}Zr-^{95}Nb 726–768 keV photopeaks with their activity in the region of 482 keV. The latter was found to be about 10% of the photopeak activity. A sample obtained by irradiation and chemical separation of zirconium oxide containing 0·5% *w/w* of hafnium oxide gave a ^{181}Hf 482 keV photopeak 10 times as intense as the ^{95}Zr-^{95}Nb 726–768 keV photopeaks (Fig. 1). This work indicated that, under the irradiation and cooling conditions used, ^{95}Zr-^{95}Nb activity contributes less than 1% to the intensity of the ^{181}Hf photopeak, even when the Zr/Hf ratio is as high as 100. No correction was made in the present work for this small contribution but a correction, based on the ^{95}Zr-^{95}Nb intensity at 726–768 keV, could easily be made if required.

RESULTS

Full details of the results for hafnium are given in Table I. Agreement between duplicate determinations is generally quite good, the coefficient of variation showing an average of about 5% for the bulk of the determinations and rising to about 7% overall. This higher value is mainly due to poor duplication in samples 597(6·6, 4·3 ppm Hf) and 611(3·9, 6·0 ppm). The error in counting is ±2%, and the error due to inhomogeneity of the neutron flux is estimated to be about ±3%. The remaining error arises in the chemical separation, *e.g.*, from radiochemical impurities and the yield determination.

The average value of 5·3 ppm hafnium found by us for standard rock G-1 is in good agreement with the neutron-activation value of 5·0 ppm reported by Setser and Ehman[2] and the mass-spectrographic results of 5 and 5·2 ppm reported by Brown and Wolstenholme[5] and Taylor[6] respectively. Morris and Slater[7] record an average of 7·6 ppm hafnium in G-1 by neutron-activation analysis.

The values for zirconium reported in Table I are the averages of replicate analyses made by a previously described X-ray fluorescence spectrographic method.[8,9] Results for the Malsburg granite have been published elsewhere[10] and those for the Schluchsee and Bärhalde granites are from unpublished theses.[11,12]

GEOCHEMICAL DISCUSSION

The almost identical chemical properties of zirconium and hafnium are reflected in the very close geochemical coherence between the two elements. Hafnium, 1/10–1/100 as abundant in geological materials as zirconium, does not form minerals of its own but occurs in zirconium-bearing minerals. In calc-alkali rocks most of the zirconium and hafnium occur in zircon and, as a result, the Zr/Hf ratios of the whole rocks and the separated zircons are usually the same. Previous workers[13–17] have found that the Zr/Hf ratio in both rocks and zircons decreases with progressive evolution from basic to acidic plutonic rocks, *i.e.*, the ratio decreases with decreasing age of the rocks in a genetically related sequence.

Kosterin *et al.*[13] give average values for the Zr/Hf ratios in zircon from rocks in Northern Kirgizia of 71 for gabbros, 45 for hornblende-biotite granites and 29 for hydrothermal veins. Vainshtein *et al.*[14] found ratios down to 3·2 (representing 13·8% *w*/*w* HfO_2) in zircons from a pegmatite. Kosterin *et al.*[17] observed that quickly cooled (volcanic and hypabyssal) rocks show rather irregular variation in their Zr/Hf ratios but that, in agreement with earlier work, slowly cooled magmatic rocks show a decrease in Zr/Hf ratio from basic to acidic types. Delaloye and Chessex[18] reached similar conclusions, reporting average values of Zr/Hf for zircons from tonalite-monzonites, granodiorites, calc-alkali granites and alkali granites of 42·5, 39·3, 37·3 and 32·9 respectively.

In the present work we have investigated samples from three different granite masses of the Southern Black Forest, Germany. The Malsburg granite (GM), of Lower Carboniferous age, is a biotite granite with hornblende present in some parts. The Schluchsee granite (GSch) is Upper Carboniferous in age and is a biotite granite, free from hornblende but sometimes bearing muscovite. The Upper Carboniferous Bärhalde granite (GBH) is a typical two-mica granite, more acid than the other two. GSch and GBH are adjacent to each other and GM lies 30 km to the SW, being separated from the two other bodies by older crystalline rocks.

Previous geochemical investigations[10–12,19] of samples from 70–100 localities within each body showed that in the succession GM–GSch–GBH the mean zirconium and titanium contents decrease while the mean rubidium contents increase. The same workers also observed that each individual pluton shows the effects of differentiation, there being strong variations in the concentrations of a number of elements and the amounts of accessory and essential minerals during progressive crystallization from the margin to the core. Thirty-one of the samples used in the previous work have been selected for the present study.

The results (Table I) show a decrease in the Zr/Hf ratio from 35 to 10 as zirconium and hafnium decrease from 280 and 9 ppm to 30 and 3 ppm respectively (ignoring the high hafnium values of 16·5 and 15·1 ppm for sample numbers 484 and 466). There is a direct relationship between the Zr/Hf ratio and zirconium contents of the rocks. In these calc-alkali granites the minerals zircon and biotite are more abundant in the earlier crystallized rocks, whereas potash feldspar is more abundant in the later rocks. These observations account for the decreasing zirconium and titanium and increasing rubidium contents as crystallization progresses, explaining why these elements are good indicators of the differentiation processes taking place. Figure 2 shows the relationship between the Zr/Hf ratio and the index elements titanium and rubidium and indicates that the Zr/Hf ratio tends to decrease steadily with progressive differentiation, both within the individual plutons and in the sequence GM–GSch–GBH. The general levels of zirconium, hafnium and the Zr/Hf ratio are lowest in the most acidic (GBH) of the three masses. Thus the Zr/Hf ratios can be correlated with the previously known geochemical and petrographic data for the three granites.

Various authors have tried to explain why the Zr/Hf ratio decreases during differentiation. Ahrens[20] has pointed out that the properties of simple zirconium and

TABLE I.—RESULTS FOR ZIRCONIUM AND HAFNIUM

Pluton	Sample no.	Zr,* *ppm* average	Hf, *ppm*†	Hf, *ppm* average	Zr/Hf, *w/w*
Malsburg	197	284	8·3	8·3	34·3
	21	281	9·9, 8·4	9·1	30·9
	69	210	6·7, 7·5	7·1	28·6
	70	207	5·4, 7·0	6·2	33·4
	128	206	8·3, 8·2	8·2	25·2
	65	184	7·2; 8·0, 7·3	7·5	24·6
	125	183	5·1, 4·3	4·7	39·6
	54	175	6·9, 6·4	6·6	26·6
	66	166	6·5, 6·4	6·4	25·9
	20/7	155	5·6, 7·0	6·3	24·6
Schluchsee	445	231	8·1	8·1	28·5
	474	220	6·9	6·9	31·9
	473	207	9·6	9·6	21·6
	507	195	8·0	8·0	24·4
	497	178	9·1, 8·1	8·6	20·7
	484	159	17·6; 15·4, 16·2	16·4	9·7
	515	130	5·8, 5·2	5·5	23·6
	486	120	6·3	6·3	19·1
	598	116	4·8, 5·6	5·2	22·3
	608	101	6·0, 5·4	5·7	17·7
	457	97	6·5, 5·3	5·9	16·4
	466	81	15·1	15·1	5·4
Bärhalde	597	114	6·6, 4·3	5·4	21·1
	620	100	5·8, 5·7	5·8	17·2
	611	69	3·9, 6·0	5·0	13·8
	621	60	4·5	4·5	13·3
	581	52	3·4, 3·6	3·5	14·8
	479	41	6·2, 5·0	5·6	7·3
	208/215	38	4·0, 4·5	4·2	9·0
	577	33	2·9, 3·8	3·4	8·7
	616	33	3·9, 4·3	4·1	8·0
U.S.G.S. Standard G-1		210	5·2, 5·4	5·3	39·7

* Determined by X-ray fluorescence spectrography.

† Results separated by a comma are duplicates from the same irradiation, those by a semicolon are from a different irradiation.

hafnium compounds, *e.g.*, oxides and fluorides, indicate that Zr–anion bonds are slightly more covalent in character than the corresponding Hf–anion bonds and that this factor should cause the Zr/Hf ratio to rise during differentiation, which is opposed to the observations. Butler and Thompson[4] discuss the possibility that partial separation of the two elements could be caused by the fractionation of volatile halides. Taylor[21] says that the trend of the Zr/Hf ratio indicates that the Hf-O bond is slightly more covalent than the Zr-O bond and that this is to be expected from the values of the first ionization potentials (6·84 eV for Zr and 7 eV for Hf). However more recent data[22] show that the first ionization potentials are 6·95 and 5·5 eV for Zr and Hf respectively.

Burns and Fyfe[23,24] have recently discussed reasons why the existing rules and principles used to explain geochemical behaviour are unsatisfactory and they stress the need for consideration of all the thermodynamic quantities involved when crystals form from a melt. The structure and chemical composition of the melt, as well as of the crystal, must be considered since they contribute to the energy of the system. It

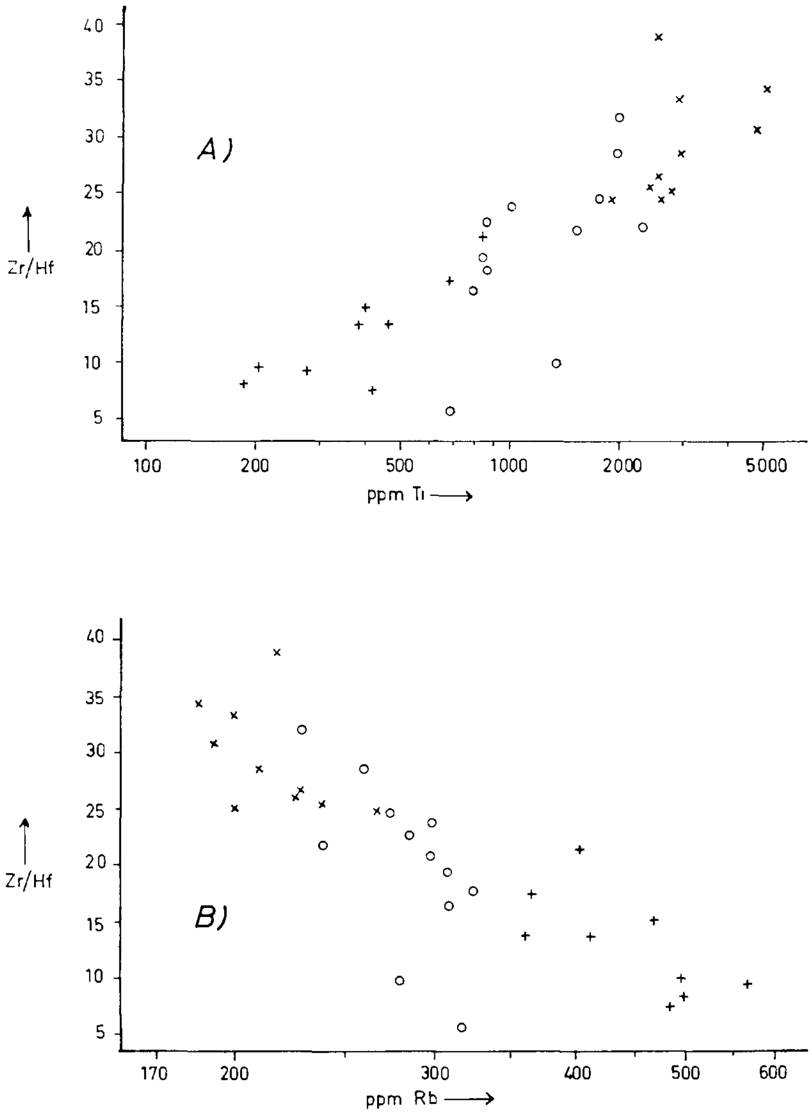

Fig. 2.—Zr/Hf ratios plotted (*A*) against Ti and (*B*) against Rb contents. ×-Malsburg Granite (GM); ○-Schluchsee Granite (GSch); +-Bärhalde Granite (GBH)

has also been pointed out that the introduction of some covalent character into an ionic bond strengthens the crystal lattice,[23,24] contrary to statements sometimes made by geochemists. This additional energy can be considered as a polarization energy term in the lattice energy equation for ionic crystals.[25]

Whittaker[26] has suggested that a silicate melt approximates to a random close-packing of oxygen ions, with the silicon and other cations occupying the available interstitial sites. It is known that the proportion of tetrahedral sites in natural silicate liquids increases with increasing amounts of alkali silicate,[27] resulting in a corresponding decrease in the number of octahedral, and larger, sites. This would tend to force 6-co-ordinate cations in the melt into energetically unfavourable lower-co-ordination sites. The alternative would be for these cations to leave the melt and enter the crystal phase, where there is a higher proportion of octahedral sites. Zr^{4+} and Hf^{4+} ions are too large (0·79 Å)[20] to enter tetrahedral sites and we suggest that the distribution of these elements between melt and crystals is governed mainly by the proportion of octahedral sites and the concentrations of the two elements in the melt.

TABLE II.—UNIT CELL VOLUMES OF SOME CORRESPONDING Zr AND Hf COMPOUNDS

Compound	Unit cell volume, Å^3 X = Zr	X = Hf
XBr_4	1313	1299
XC	103·6	100·0
XN	94·82	91·13
XO_2	140·6	131·1
XP	441·6	428·1
XS_3	165·7	162·9
$XSiO_4$	260·5	255·2

Table II gives unit cell volumes of a number of corresponding zirconium and hafnium compounds. In each case the hafnium has a smaller unit cell, indicating that Hf^{4+} occupies somewhat less space than Zr^{4+} in these structures. We propose that this property of Hf^{4+} gives it a slight stabilization, relative to Zr^{4+}, in the melt as the proportion of octahedral sites decreases during differentiation. On the basis of this hypothesis the Zr/Hf ratio should decrease as differentiation proceeds. Similar factors may explain the distribution of these elements between alkali amphibole and zircon in alkali and undersaturated alkali rocks.

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Zusammenfassung—Eine ziemlich rasche Methode zur Abtrennung von Hafnium aus bestrahlten Gesteinsproben wird beschrieben und Ergebnisse von Hafniumbestimmungen mitgeteilt. Die Verteilung von Zirkonium und Hafnium sowie die Veränderung des Zr/Hf-Verhältnisses in drei Kalk-Alkali-Granitmassen werden diskutiert. Gründe für das beobachtete Abnehmen des Zr/Hf-Verhältnisses beim Kristallisieren schmelzflüssiger Gesteine werden vorgeschlagen.

Résumé—On décrit une méthode moyennement rapide pour la séparation du hafnium d'échantillons de roche irradiés et rapporte les résultats des dosages du hafnium. On discute de la répartition du zirconium et du hafnium et de la variation du rapport Zr/Hf dans trois masses de granit alcalino-calcaire. On suggère des raisons pour la décroissance observée dans le rapport Zr/Hf durant la cristallisation des roches ignées.

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SEPARATION SCHEME FOR THE DETERMINATION OF ALKALI METALS (K, Rb, Cs), ALKALINE EARTHS (Sr, Ba) AND RARE EARTHS (Ce, Nd, Sm, Eu) IN SILICATE MATERIALS BY ISOTOPIC DILUTION ANALYSIS

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Summary—A scheme is outlined for the separation of Li, K, Rb, Cs, Sr, Ba, Ce, Nd, Sm and Eu from silicate materials. The elements are separated by cation-exchange to provide groups suitable for mass spectrometric analysis, and are then further purified by anion-exchange. Results obtained by isotopic dilution analysis are reported for G-1, W-1, and the Barwell meteorite—in these measurements the alkali metals were determined separately from the other elements. Requirements are discussed for combining the procedures to form a more comprehensive method for use with a single sample.

NEUTRON-ACTIVATION analysis and mass spectrometric isotopic dilution are well-established methods for the accurate determination of trace elements, but they are frequently restricted to the study of only a few elements in any given sample. A more comprehensive approach offers two main advantages: (*a*) it provides for greater economy both in effort and sample material; (*b*) the significance of results, for example for geochemical studies, often centres on element correlations, and a scheme providing for the simultaneous measurement of many elements can reduce uncertainties otherwise caused by inhomogeneities between different samples of the same material.

Recent papers from this laboratory[1,2] outlined a radiochemical separation scheme for the measurement of eleven elements by neutron-activation analysis. The present paper centres on those elements that are particularly appropriate to the "stable" isotopic dilution technique. Earlier work covered the separation of rubidium and caesium from meteorites,[3] rubidium and strontium for geological age measurements, *etc.* These methods are now extended to include a wider range of alkali metals, alkaline earths and rare earths. The following sections outline the basis of a complete separation scheme for ten elements, results obtained for nine of these while various parts of the scheme were being tested, and further steps needed to provide a single integrated procedure.

EXPERIMENTAL

The aim of the chemical separation is to divide the elements into groups, each suitable for isotopic analysis by mass spectrometry. In the earlier work, after addition of isotopically enriched tracers

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and dissolution of samples, cation-exchange chromatography was used to separate rubidium and caesium from calcium, and rubidium from strontium. In the present separation alkali metals are again eluted from Zeo-Karb 225 with 2·5*M* hydrochloric acid to give fractions containing lithium, potassium, rubidium and caesium for combination as required. As a development of the scheme outlined by Fritz and Garralda,[4] the eluent is then changed to 2·1*M* nitric acid to give a strontium and barium fraction, and then to 2·6*M* nitric acid for the rare earth group. Each of the fractions is then further purified by anion-exchange on a column of De-Acidite FF in the oxalate form for the alkali metals, and the chloride form for the other two groups of elements. Contamination arising during the procedure or from various reagents is determined, as required, by processing a solution of tracer only.

Isotopic analyses were made with two thermal emission mass spectrometers. Rare earths were determined with a standard AEI MS5 instrument. The remaining elements were determined with a "home-built" 150-mm radius 60° instrument: a plate detector, vibrating reed electrometer and chart recorder were used for the measurement of lithium and potassium; electrostatic scanning was used for the other elements—the output from the electron multiplier was digitized with a Hewlett-Packard 2211 voltage-frequency convertor, and successive sweeps were accumulated in a Laben 512-channel multiscaler. Potassium, rubidium and caesium were ionized with a single platinum filament, and lithium by the nickel side-flag technique.[5] Triple filament (tungsten) units were used for the other elements.

The separated isotopes used as tracers for all elements except caesium and europium were obtained from the Harwell Electromagnetic Separation Group, and had the following concentrations for the main isotope: ^{6}Li, 99·98%; ^{41}K, 95·3%; ^{87}Rb, 99·6%; ^{84}Sr, 51·0%; ^{134}Ba, 64·4%; ^{142}Ce, 95·8%; ^{145}Nd, 76·9%; ^{149}Sm, 90·5%. ^{151}Eu, 99·1%, was obtained from the Oak Ridge National Laboratory, and fission-product caesium from the Radiochemical Centre, Amersham. These were dissolved and diluted to suitable concentrations ranging from 0·1 mg/g for ^{41}K to 0·01 μg/g for ^{151}Eu. The concentration of each tracer solution was determined by isotopic dilution against dilute standard solutions prepared from Johnson-Matthey "Specpure" reagents. Reagents (with drying temperatures) were KCl (500°), RbCl (200°), CsCl (300°), $SrCO_3$ (460°), $BaCO_3$ (460°), CeO_2 (700°), Nd_2O_3 (640°), Sm_2O_3 (600°), Eu_2O_3 (650°). The mean deviations for these measurements of tracer concentrations ranged from 0·4% to 3%, with a mean value of 1·2% for the nine elements.

Reagents

Hydrochloric acid. Distilled in quartz from analytical grade-reagent.

Nitric acid. Distilled in quartz from lead-free reagent under reduced pressure.

Sulphuric acid. Distilled in quartz from lead-free reagent.

Perchloric acid. Distilled in quartz from lead-free reagent.

Hydrofluoric acid. Distilled in PTFE from analytical-grade reagent.

Apparatus

Quartz, polythene or platinum wherever possible. Platinum slides made from sheet metal, with a small indentation near one end.

Preparation of ion-exchange columns

Cation-exchange column. Zeo-Karb 225, <200 mesh, washed with 6·2*M* hydrochloric acid and air-dried. Add 16 g as a slurry in 6·2*M* hydrochloric acid to a polythene tube, drawn out at one end. Wash with ~100 ml of 6·2*M* hydrochloric acid and ~200 ml of 2·5*M* hydrochloric acid. Plugs of cotton wool, not silica wool, should be used.

Anion-exchange column. Use 2 g of De-Acidite FF in a polythene tube. For the oxalate form wash with ~25 ml of 2·5*M* hydrochloric acid, ~25 ml of saturated oxalic acid, ~25 ml of hydrochloric acid, ~20 ml of water, ~25 ml of saturated oxalic acid, ~20 ml of water. For the chloride form wash with ~40 ml of 6·2*M* hydrochloric acid.

Separation procedure

Weigh out the tracers individually, evaporate each to dryness; weigh out the sample (~100 mg). Add 5 ml of hydrofluoric acid and preferably leave to stand overnight. Evaporate, add 5 ml each of hydrofluoric and perchloric acids and evaporate again. Add a further 5 ml of perchloric acid and evaporate to decompose fluorides. Finally add ~0·5 ml of water and evaporate to dryness. Dissolve the residue in 2 ml of 2·5*M* hydrochloric acid. (*Note.* It may first be necessary to add about 1 ml of 6·2*M* hydrochloric acid and evaporate just to dryness, to ensure complete dissolution.) Transfer to the cation-exchange column, add ~1 ml of 2·5*M* hydrochloric acid, and then 5 ml more, in each case allowing the column to drain, and then connect to the reservoir. Adjust the flow rate to ~1 ml/min, elute and collect as follows.*

Elution with 2·5M *hydrochloric acid*

0–20 ml	discard	
20–30 ml	collect	Li
30–50 ml	discard	
50–100 ml	collect	K, Rb, Cs

Remove the hydrochloric acid from the top of the column, rinse the reservoir, pass 30 ml of water through the column, and then continue elution with 2·07*M* nitric acid.

Elution with 2·07M *nitric acid*

100–120 ml	discard	
120–240 ml	collect	Sr, Ba
240–260 ml	discard	

Remove the nitric acid from the top of the column, rinse the reservoir and continue elution with 2·58*M* nitric acid.

Elution with 2·58M *nitric acid*

260–460 ml	collect	Eu, Sm, Nd, Ce

Evaporate each fraction to dryness in a clean platinum dish.

Li *fraction.* Add 1 ml of water to dissolve the residue, and add to a De-Acidite FF column in the oxalate form. Elute with 10 ml of water, and evaporate in the same platinum dish. Transfer to a microscope slide treated with "Repelcote". Add *1 drop* of conc. nitric acid, evaporate and transfer in water to a nickel "flag" assembly for mass analysis.

K, Rb, Cs *fraction.* As for Li but transfer to a platinum slide, add *1 drop* of conc. sulphuric acid and evaporate. Transfer to a precleaned single platinum filament for mass analysis.

Sr, Ba *fraction.* Evaporate in a platinum dish, add 1 ml of 6·2*M* hydrochloric acid, warm and transfer to a De-Acidite FF column in the chloride form. Elute with 10 ml of 6·2*M* hydrochloric acid, and collect and evaporate in the same platinum dish. Flame to red heat to remove any organic residue. Transfer to a microscope slide treated with "Repelcote", using hot conc. nitric acid.

Ce, Nd, Sm, Eu *fraction.* As for Ba and Sr, but after flaming, extract the rare earths with hot conc. sulphuric acid and transfer to a platinum slide. After evaporation *just* to dryness, load on to a precleaned filament with dilute sulphuric acid.

RESULTS

The results listed in Table I were determined by the procedures above except that lithium was omitted, and potassium, and rubidium and caesium were determined separately from the other elements. In the comparison with earlier data, the accuracy of the new set of results is dependent on the following factors: (*a*) the precision of the measurements—the mean deviation ranges from <1% to a worst case of ~8% for caesium in Barwell at 0·012 ppm; the average value of the mean deviation for all results is ~2%; (*b*) the calibration of the tracer—again mean deviations range from 0·4 to 3% with a mean value of only 1·2%; results for strontium are, however, subject to a further uncertainty of 10% in the concentration of the standard used; (*c*) blank corrections—for the results above, the corrections were small, usually 0·1–1%, occasionally 2–4% for a few very low concentrations, and the uncertainties insignificant.

For G-1 and W-1 there is satisfactory agreement with accepted or published values. For Barwell there are few published results, but the observed values are close

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* Elution volumes must be redetermined for each batch of resin.

TABLE I.—RESULTS FOR STANDARD ROCKS G-1 AND W-1, AND THE BARWELL CHONDRITE

Element	Individual results	Mean value	Comparison values
Standard Diabase W-1			
K	0·51, 0·53	0·52%	0·52[a], 0·53[b]
Rb	21·2, 20·6	20·9 ppm	20·1[a], 21·3[c], 22·5[m]
Cs	1·05, 1·02	1·04 ppm	0·83[d], 1·08[c]
Sr*	187, 185	186 ppm	172[e1], 180[e2]
Ba	147, 147	147 ppm	134[a], 158[f]
Ce	23·7, 23·5	23·6 ppm	15·1[g], 21[d], 23·6[h], 24[i], 24·3[j]
Nd	13·7, 13·4	13·5 ppm	15·08[h], 15·1[j], 20·2[g], 21[i]
Sm	3·4, 3·6	3·5 ppm	2·8[d], 3·2[k], 3·4[l], 3·46[g], 3·76[h], 3·78[i], 3·79[j]
Eu	1·15, 1·15	1·15 ppm	1·04[i], 1·08[d], 1·09[j], 1·123[h], 1·2[l], 1·29[g]
Standard Granite G-1			
K	4·63, 4·55	4·59%	4·2[d], 4·52[b], 4·58[a]
Rb	not determined		—
Cs	1·46, 1·41	1·44 ppm	1·5[c]
Sr*	234, 228	231 ppm	236[e2], 252[e1]
Ba	980, 983	982 ppm	1075[a], 1040[f]
Ce	166, 181	174 ppm	134[j], 150[g], 156[i], 157[l], 173[h]
Nd	55, 60	58 ppm	44[i], 54·6[j], 55·2[g], 86·4[h]
Sm	8·2, 8·4	8·3 ppm	7·52[i], 7·6[l], 7·7[k], 8·25[g], 8·6[j], 8·89[h]
Eu	1·28, 1·28	1·28 ppm	1·04[i], 1·04[j], 1·24[h], 1·3[l], 1·36[g]
Barwell Chondrite†			
K	0·080, 0·081	0·081%	0·080[n]
Rb	2·5, 2·4, 2·4	2·41 ppm	
Cs	0·011, 0·010, 0·013	0·011 ppm	
Sr*	9·7, 10·0	9·9 ppm	
Ba	3·8, 3·5	3·6 ppm	
Ce	0·88, 0·87	0·88 ppm	
Nd	0·65, 0·66	0·65 ppm	
Sm	0·20, 0·21	0·21 ppm	
Eu	0·076, 0·077	0·076 ppm	

[*] Results for Sr are subject to an uncertainty of 10%.

[†] Results refer to total meteorite.

[a] Ingamells and Suhr,[6] spectrochemical analysis.

[b] Fleischer and Stevens,[7] review of data.

[c] Cabell and Smales,[8] activation analysis.

[d] Gordon *et al.*,[9] instrumental activation analysis.

[e] Loveridge *et al.*,[10] *e*1, activation analysis *e*2, isotopic dilution.

[f] Schnetzler *et al.*,[11] isotopic dilution.

[g] Towell *et al.*,[12] activation analysis.

[h] Schnetzler *et al.*,[13] isotopic dilution.

[i] Tomura *et al.*,[14] activation analysis.

[j] Haskin and Gehl,[15] activation analysis.

[k] Brunfelt and Steinnes,[16] instrumental activation analysis.

[l] Cobb,[17] instrumental activation analysis.

[m] Pinson *et al.*,[22] isotopic dilution.

[n] Moss *et al.*,[19] flame photometry.

to those expected for this class of meteorite. For potassium the concentration for the total meteorite is 0·081% in close agreement with the value of 0·080% determined by flame photometry at the British Museum,[19] and in contrast with earlier higher values (average value for chondrites[21] is 0·083%); rubidium and caesium are close to the median values recorded for a range of hypersthene meteorites[3] (Rb, 2·7 ppm; Cs, 0·077 ppm); for the rare earths Haskin *et al.*[20] report mean values of Ce 1·19 ppm, Nd 0·63 ppm, Sm 0·22 ppm, Eu 0·083 ppm, determined by activation for a range of "ordinary" chondrites.

DISCUSSION

In development of the procedure a number of difficulties were encountered from contamination problems. Barium was a particularly troublesome impurity, but could be controlled by purification of reagents. For example the batch of "Transistor Grade" hydrofluoric acid used contained ~0·2 μg of Ba/ml, but this fell to 0·00025 μg/ml on distillation in PTFE. The various impurities contained in the isotopically enriched materials used as tracers formed a more serious potential source of error. Since tracers are prepared by electromagnetic separation, impurities could have an unnatural isotopic composition and so might be incorrectly determined, or even not detected by a normal blank correction. This is particularly important for the ^{41}K tracer which may be added in a 10^2–10^5-fold excess over the other elements. Relevant impurities were detected in the lithium and potassium tracers by thermal emission studies, and so, for the measurements reported in Table I, lithium was omitted from the scheme, and potassium, and rubidium and caesium were determined separately from the other elements. For the group of strontium, barium, cerium, neodymium, samarium and europium, each tracer was examined by spark source mass spectrography, and the concentrations of the other five elements were shown to be insignificant.

In this work the alkaline earth and rare earth elements were measured with different mass spectrometers, but only to provide greater experience for one of the authors while on attachment at A.E.R.E. Further tests have shown that these elements can readily be determined in a single mass analysis by using both side-filaments of a triple filament source unit; it is however preferable to examine the alkali metals by a separate isotopic analysis.

The overall scheme outlined in this paper has been tested through to the mass analysis stage, and given tracers of adequate purity can provide a method for the determination of the ten elements Li, K, Rb, Cs, Sr, Ba, Ce, Nd, Sm and Eu on a single sample; this would involve three mass analyses: (*i*) Li, (*ii*) K, Rb, Cs, (*iii*) alkaline earths and rare earths loaded on separate side-filaments of a single source unit. The method could be extended if required to include some other elements, for example only four rare earths were selected for study, but Schnetzler *et al.*[13] describe a procedure for measuring nine rare earths, based on two isotopic analyses. It is also expected that the scheme would be integrated with measurements made by instrumental activation analysis of intact samples before dissolution for isotopic dilution work. For example this could provide a means for measuring sodium, for which there is no convenient tracer for mass spectrometry, in order to complete the coverage of the alkali metals.

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Zusammenfassung—Ein Trennungsgang für Li, K, Rb, Cs, Sr, Ba, Ce, Nd, Sm und Eu in Silikaten wird skizziert. Die Elemente werden durch Kationenaustausch in Gruppen aufgetrennt, die zur massenspektrometrischen Analyse geeignet sind, und dann weiter durch Anionenaustausch gereinigt. Durch Isotopenverdünnungsanalyse erhaltene Ergebnisse werden für G-1, W-1 und den Barwell-Meteoriten angegeben-bei diesen Messungen wurden die Alkalimetalle getrennt von den anderen Elementen bestimmt. Die Erfordernisse zur Kombination der Verfahren werden diskutiert, um eine umfassendere Arbeitsvorschrift zur Analyse einer einzelnen Probe zu erhalten.

Résumé—On ébauche un schéma pour la séparation de Li, K, Rb, Cs, Sr, Ba, Ce, Nd, Sm et Eu à partir de substances silicatées. Les éléments sont séparés par échange de cations pour fournir des groupes convenant pour l'analyse spectrométrique de masse, et sont purifiés davantage par échange d'anions. On mentionne les résultats obtenus par analyse par dilution isotopique pour G-1, W-1 et la météorite de Barwell—dans ces mesures les métaux alcalins ont été dosés séparément des autres éléments. On discute des conditions nécessaires pour combiner les techniques afin de former une méthode plus générale pour l'emploi avec un seul échantillon.

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POTASSIUM-ARGON DATING OF THE CAPE GRANITE AND A GRANITIZED XENOLITH AT SEA POINT

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Summary—Ages obtained by potassium-argon dating are reported for the total rock, light mineral fraction and heavy mineral fractions of the Cape Granite, and of a granitized xenolith derived from the Malmesbury sediments. These ages lie between 430 and 554 million years. The heavy mineral fractions from each rock type show the oldest age, 540 (granite) and 554 (xenolith) million years. These ages are interpreted as lower limits, and the granite age confirms the age of 553 million years found by rubidium-strontium dating. The coincidence of the ages of the different fractions of the granite and xenolith samples is discussed in the light of the different suggestions about the age of the Malmesbury sediments. The conclusion is reached that all pre-granitization history has been eliminated. The possibility of the use of argon retention as a measure of metamorphic activity is suggested.

ALDRICH *et al.*[1] reported isotopic age measurements made by rubidium-strontium and potassium-argon methods on biotite, and by uranium-lead and thorium-lead methods on zircon, from a single sample of the normal granite from the Cape Peninsula, South Africa. The results obtained varied from 330 × 10^6 yr (^{238}U–^{206}Pb on zircon) to 600 × 10^6 yr (Rb–Sr on biotite). Allsopp and Kolbe[2] determined the age of emplacement of the granite, by using the rubidium-strontium method, hoping that the primary isotopic ratio, ^{87}Sr/^{86}Sr, obtained in the course of their study, might be useful in providing further evidence on the possibility that the granites were derived by mobilization of the Malmesbury sediments which are invaded by stocks and plutons of the Cape granite. They reported an age of 553 × 10^6 yr for the total rock age of the granite, and mineral ages which were essentially in agreement with this age but which suggested that a mild metamorphism had caused some loss of daughter-product from biotites and potassium feldspars. They also reported ages obtained by the potassium-argon method for two biotite samples from the granite, which varied between 487 and 496 × 10^6 yr, and which were lower than the ages they obtained for the same samples by the rubidium-strontium method. Since the primary ^{87}Sr/^{86}Sr ratio of the granite was not unusually high, as would have been the case had the granite been derived from the presumably much older Malmesbury sediments, Allsopp and Kolbe attempted to measure the age of the Malmesbury sediments by rubidium-strontium determinations on total rock samples. The isochron obtained was linear, indicating an age of 595 ± 45 × 10^6 yr, and they concluded that the age of the Malmesbury deposition could not "greatly exceed the apparent age" obtained from the isochron.

All radiometric age determinations depend on four assumptions. First, that the decay of parent to daughter isotope proceeds at a constant known rate. Second, that the sample to be dated contained, at the time of its formation, either an amount of daughter isotope which can be determined at the present time, or else no daughter isotope at all. Third, that the time taken for formation of the sample was short compared with its present age. Last, that the sample has remained a closed system with respect to both parent and daughter isotope since the time of its formation.

In the case of the $^{40}K/^{40}Ar$ dating method, this last assumption is often not valid. That argon loss by diffusion is possible was suggested by Gentner *et al.*[3,4] The quantity lost will depend on the grain size and the structure of the particular potassium-bearing mineral involved. Lower $^{40}Ar/^{40}K$ ratios are usually found for feldspars than for co-existing biotites, and this discrepancy is normally attributed to the greater rate of diffusion of argon out of feldspars than out of biotites. Loss of argon by steady diffusion out of a crystal would not, however, lead to the determination of an erroneous total rock age unless the argon was lost to the system as a whole. By system, here, we must understand a volume of rock which is eventually all used as a sample for analysis, and from which no argon has been lost, although internal diffusion of argon may have occurred. It was to overcome the effect of daughter isotope migration in rubidium–strontium age determinations that the total rock approach was introduced.[5]

The validity of an age determined by the potassium–argon method will also depend on the behaviour of the parent isotope, ^{40}K, throughout the life of the rock. Since the mineral containing potassium incorporates it on being formed, the parent isotope is not foreign to its host mineral, and there might appear to be no reason to expect potassium escape or addition, nor to expect any marked variation in the isotopic abundance of ^{40}K in this potassium. The importance of potassium movement in the granitization process has long been recognized, however, and recent work has shown that diffusion of potassium into rocks[6–8] occurs even when granitization has not taken place. This movement of potassium results in variation in the isotopic ratio $^{39}K/^{41}K$. $^{39}K/^{41}K$ ratios vary for total rock samples of different granites[9–12] and, in addition, it is known that different mineral fractions of granites show different $^{39}K/^{41}K$ ratios.[8,13] It therefore does not seem reasonable to expect that the abundance of ^{40}K remains constant throughout nature, although it should be remembered that the observed variations in $^{39}K/^{41}K$ ratio are small (up to 3 %) and that any variation in ^{40}K abundance would be even smaller. Nevertheless, ^{40}K concentrations are generally obtained by measurement of the total potassium concentration in a sample, and use of the assumed constant abundance of ^{40}K in nature. This assumption is supported by ^{40}K abundance measurements[10] on a number of samples, including some which show differing $^{39}K/^{41}K$ ratios.

Although the available evidence indicates that the abundance of ^{40}K may be constant in nature, the non-isolation of systems with respect to their potassium content is irrefutable in view of the interpretation of varying $^{39}K/^{41}K$ ratios in terms of movement of potassium. The introduction or removal of potassium from a rock sample is likely to have a very much greater effect on the measured age than any minor variations in the abundance of ^{40}K which may occur as a result of this movement, because it is assumed that the present potassium content of a sample is that of the initial sample on its formation less that lost by natural decay. Thus, if potassium was added to a rock during its lifetime, the ratio $^{40}Ar/^{40}K$, measured for that sample at some time after introduction of the potassium, would be lowered and the measured age for such a sample would therefore be too low.

In contrast to the problem of inaccurate ages caused by a steady diffusion of argon from a mineral, there is the possibility of a catastrophic loss of argon as the result of metamorphism of the system containing it. If such an event occurs, and loss of argon is complete, then the rebirth of the rock may be accurately dated. If loss of argon is not complete at the time of metamorphism then there can be no method of determining, by $^{40}Ar/^{40}K$ ratios, either the age of the original formation of the date of the metamorphic event. Thus, while argon loss by steady diffusion causes a measured age to be only a lower limit of the age of the sample, incomplete loss of argon during metamorphism would lead to an age intermediate between that of the original formation and that of the metamorphic event.

While potassium–argon measurements on a system which has undergone such change are of no value for obtaining a meaningful age, they could prove useful in attempts to gauge the intensity of a metamorphic event. Assume that a pre-existing rock is measurably older than an intruding granite. Assume also that the intrusion of the granite causes some metamorphism of the pre-existing rock. Then the amount by which the apparent age of the metamorphosed rock exceeds the age of the granite will vary inversely with the intensity of the metamorphic process.

The work described in this paper represents an attempt to data the Cape Granite by the potassium–argon method and to obtain information on the possible retention of argon by a xenolith of Malmesbury sediment during its metamorphism by the surrounding granite. It was also hoped that, had the xenolith not released all the argon accumulated during its existence as a sediment, it might be possible to obtain some indication of the intensity of the metamorphic process.

EXPERIMENTAL

Samples

The samples analysed were a sample of the Cape Granite, GI, and a sample taken from the edge of a granitized xenolith, GXI, found in this granite. Both the samples and their location have been previously described[13] and have been used for $^{39}K/^{41}K$ ratio studies.[6,8]

In the sample numbering system the letters T, L and H after the sample number represent "total rock", "light mineral fraction" and "heavy mineral fraction" samples respectively.

Representative samples of the original hand-specimens were crushed in a stainless steel mill until the whole passed a 40-mesh sieve. After mixing, the sample for analysis was withdrawn and crushed to pass an 80-mesh Tyler sieve.

The separated fractions of the representative total rock samples were obtained by floating the crushed samples on bromoform. The heavy fraction, comprising biotite, hornblende and other heavy minerals, settled to the bottom of the liquid, while the light fraction, comprising feldspar and quartz, remained in suspension and was decanted off. Subsequent examination of the fractions showed that while the separation of light and heavy fractions was not perfect, the contribution of the impurity fraction to concentration determinations would be negligible.

Argon determination

The argon extraction apparatus was of standard design. The purification train comprised a moisture trap containing magnesium perchlorate, a carbon dioxide trap containing potassium hydroxide, and a calcium furnace to ensure reaction and removal of gases other than the noble gases. The calcium furnace was a modification of the original design of Soddy[14] and of the furnace used by Arrol and his co-workers,[15] and included a stainless steel crucible and lavite supporting parts. The samples for analysis varied in weight between 4 and 9 g, and were fused with 60 g of sodium hydroxide for 6 hr. Preliminary experiments had shown that release of argon from rock samples of this size was reproducible for heating periods of over 2 hr under these conditions. Mixing of released argon and spike argon was allowed to take place during the whole period of extraction. At the end of this time the spiked sample, after multiple passages through the calcium furnace, was trapped and transferred to the mass spectrometer for analysis.

The spikes used during this work were all prepared from a single sample of ^{38}Ar obtained from the U.K.A.E.R.E., Harwell. This sample, containing 0·168 standard ml of argon, was subdivided into 40 approximately equal samples of calibrated volume (approximately 25 ml) and measured pressure. The apparatus used was similar to that described by Haden and Inghram,[16] modified by the construction of breakseals into a manifold as used by Carr and Kulp.[17]

The ^{40}Ar in the extracted argon from each rock sample was determined by isotope dilution analysis, with a 5-in., 60°, Nier-type gas source mass spectrometer previously described by Delaney.[18] The only modification to the instrument was in the sample handling and inlet systems, so that satisfactory results could be obtained with samples of about 2 μl of argon.

Background responses at m/e 36 and 40 could not be removed completely by baking of the spectrometer. The background in this mass range was scanned 30 times before argon was admitted to the instrument, and a further 10 times after completion of the analysis and reabsorption of argon left in the mass spectrometer. The object of the last 10 scans was to check that the background in the tube was unchanged, and consequently that the nett responses at m/e 38 and 40 were exclusively due to the admitted sample. They also served to check that there were no memory effects in the mass spectrometer.

Potassium determination

The potassium contents of all samples were measured by flame spectrophotometry (Hitachi-Perkin-Elmer 193 UV-VIS spectrophotometer with the flame photometry attachment 139–0400).

Two methods of sample dissolution were used as a partial check on the carefully controlled reagent impurities. The same potassium concentration was found for any sample regardless of which method of dissolution had been employed. These methods were those of Kallmann,[19] and of Evernden and Richards.[20] Subsequent treatment of the dissolved samples was that suggested by Cooper.[21] The ^{40}K content of the sample was determined by calculation from the measured total potassium concentration by assuming a ^{40}K abundance of 0·0119%.

RESULTS AND DISCUSSION

The results obtained are shown in Table I. The reproducibility of results obtained is indicated by the inclusion of a standard deviation with each average value quoted.

TABLE I

Sample	Potassium, %	^{40}Ar, 10^{-8} *mole/g*	Sample age*, 10^6 *yr*	Significance of age differences†
GIT	5·01 ± 0·05	0·477 ± 0·019	478 ± 17	GXIT, 30%; GIL, 99%; GIH, 99%
GIL	4·91 ± 0·02	0·413 ± 0·013	430 ± 11	GXIL, 50%
GIH	5·79 ± 0·03	0·633 ± 0·022	540 ± 16	GXIH, 55%
GXIT	3·23 ± 0·03	0·301 ± 0·003	470 ± 4	GXIL, 99%; GXIH, 99%
GXIL	2·81 ± 0·04	0·244 ± 0·008	440 ± 10	—
GXIH	4·36 ± 0·04	0·491 ± 0·004	554 ± 4	—

* The age of each sample has been calculated by using a branching ratio of 0·124 for ^{40}K decay.

† The values in this column show at what level of confidence the difference between the age of the sample and that of the stated comparison sample becomes significant. It is not advisable to consider a difference as significant unless the confidence level is at least 95%.

The ^{40}K concentrations used in the calculations were obtained on the assumption of a constant abundance. In the case of the samples from GXI, it is known that there are variations in the ratio $^{39}K/^{41}K$.[8,12] Although, on this basis, it might be expected that variations in the abundance of ^{40}K could occur, any such variations would have only a small effect (about 1 %) on the calculated age. In addition, it has been reported by Harms *et al.*[10] that even where variations in $^{39}K/^{41}K$ ratios are found, the abundance of ^{40}K remains constant. In view of these facts, it seems that any error introduced by the assumption that ^{40}K has a constant abundance would be too small to affect the calculated age by a significant amount.

Although the isotope dilution technique does not depend on the retrieval of all the argon in spike and sample, it does depend on complete mixing of the spike sample with all the argon present in the rock. Thus incomplete release of argon from the rock during the fusion process would invalidate the results. The only evidence which can support the assumption of complete argon release during fusion of the sample is the essentially reproducible argon concentration obtained from the various rock samples. This may be seen from Table I. The conclusion that all the argon in a sample has been released if a constant argon yield can be obtained is commonly made by workers making geochronological studies.

The calculated ages for each sample show remarkably little spread. From a consideration of the errors involved in measuring the ^{40}Ar and ^{40}K concentrations it would be expected that the results, on the whole, should show a greater spread. That they do not can only be attributed to a "statistical chance". The ages of the three fractions of each sample (total, light, heavy) are not the same. The differences observed follow a pattern, probably due to argon loss, with the greatest loss, and therefore the youngest age, being shown by the light (feldspar and quartz) fraction. There is no means by which we can show how much argon has been lost by each fraction, and therefore the ages can serve only as a lower limit of the absolute age.

TABLE II.—AGE DETERMINATIONS ON SAMPLES FROM THE CAPE GRANITE

Sample	Method of dating	Author	Age, 10^6 *yr*
Zircon	^{207}Pb–^{206}Pb	Aldrich *et al.*[1]	530 ± 30
Biotite	K–Ar	Aldrich *et al.*	505 ± 25
Biotite	Rb–Sr	Aldrich *et al.*	600 ± 30
Biotite	Rb–Sr	Allsopp and Kolbe[8]	518–544
K-feldspar	Rb–Sr	Allsopp and Kolbe	540–551
Biotite	K–Ar	Allsopp and Kolbe	487–496
Total Rock	Rb–Sr	Allsopp and Kolbe	553 ± 8
Total Rock	K–Ar	This work	478 ± 17
Heavy fraction*	K–Ar	This work	540 ± 16

* The heavy fraction includes biotite.

The granite age

The age determined for the graphite sample is not inconsistent with previously reported ages obtained from both mineral and total rock samples from the normal granite of the Cape Peninsula. Gl is a typical sample of this granite. Some of these earlier results are shown in Table II together with two results obtained in this work.

Assuming that the heavy fraction age determined in the course of this work is higher than the total rock or light fraction ages because the heavy minerals have lost less argon than the light minerals, this determined age would still represent a lower limit for the age of the Cape Granite. The value of 540 × 10^6 yr, then, would confirm the rubidium–strontium isochron age, measured by Allsopp and Kolbe, of 553 ± 8 × 10^6 yr.

The granitized xenolith

The three ages measured on the granitized zenolith samples show the same pattern as is found for the granite. The usual explanation of the age difference between the light fraction and the heavy fraction, namely that more argon was lost from the feldspar-rich fraction, can again be applied. This must mean that the experimentally determined ages should be regarded as lower limits to the actual age of the granitization.

The coincidence of the ages of corresponding samples from the granite and granitized xenolith is most striking. The immediate and obvious interpretation is that both are, in fact, of the same age. This implies that the process of transformation of the Malmesbury sediment to a granite-like texture was sufficiently intense to expel all the argon formed during the pre-granitization life of the sediment. If this is accepted, it must also be true that any subsequent loss of argon from the xenolith and the granite was at essentially the same rate although the two rocks are by no means identical.

There is, however, the possibility that some of the pre-granitization argon was retained during the metamorphism and that, in the post-granitization period, a slightly higher rate of loss of argon from the xenolith material has compensated for the *ab initio* argon retention. If this was the case the similarity of the ages measured now would be a coincidence. However unlikely this may seem, the possibility cannot be eliminated.

Movement of the parent isotope is also possible, and the consolidated sediment may have functioned as a sponge for potassium without undergoing visible alteration. If significant quantities of potassium had entered the sediment at any time between its consolidation and the granitization of the xenolith, the effect on the measured "age" of the xenolith would be to decrease any pre-history contribution. In other words the lapse of time between the consolidation of the sediments and the granitization would appear shorter and the probability of age measurements on granite and granitized xenolith being indistinguishable would be increased. Only large quantities of introduced potassium would, however, be sufficient to swamp the "pre-history" period completely.

One further possible explanation of the age coincidence exists. If the Malmesbury shales were laid down only shortly before being intruded by the Cape Granite, the conclusion that the metamorphism was intense enough to drive out all pre-granitization argon may be unnecessary. The consolidation of the sediment might itself involve the loss of all pre-consolidation argon and, if the time difference between consolidation and granite intrusion were small, it would be expected that the ages of the granite and the granitized xenolith would be found to be the same no matter how mild the subsequent metamorphism had been. It is essential that, if any interpretation involving the intensity of the metamorphic process is to be made, there should be a significant lapse of time between the consolidation of the sediment and the granitization process.

Although the Malmesbury shales were originally correlated with some of the older geological formations, more recent field work has tended to show that they are much younger than this.[23,24] Allsopp and Kolbe[2] have made measurements of five samples of the sediments. (These were necessarily "total rock" ages since these sediments are extremely fine-grained.) This led them to attribute an age of 595 ± 45 × 10^6 yr to the sediments. This age, together with the value of 553 × 10^6 yr determined for the granite by the rubidium–strontium method, and the interpretation of the ages for the granite presented in this paper as lower limits, might indicate that the difference in age between the sediment consolidation and the granite intrusion was very small. This would result in the determined ages for the granite and the granitized xenolith being the same. If the small difference between the sediment "age" and the granite emplacement is accepted, no conclusion can be reached about the intensity of the metamorphism in the granitization process.

There is, however, some doubt about the meaning of an "age measurement" on sediments. Although Allsopp and Kolbe are very cautious about a definite interpretation, they do, on the basis of an apparent "isochron"*, suggest that the sediments cannot be much older than their determined "age".

An over-simplified model of sediment formation may be used to show that the collinearity which leads to an apparent "isochron" for a sediment can arise when there is no possibility that a "measured age" is anywhere near the true age. Consider the erosion of an older rock which has in it two component minerals having significantly different parent/daughter ratios. (In the case of a granite we might consider the rubidium/strontium ratios in feldspar and micas.) Any sediment derived from the consolidation of this eroded material will contain regions with different amounts of the two components. It will then be possible to find significant variations in the parent/daughter ratio in different parts of the sediment, and hence different abundances of radiogenic daughter. If, during the transport of this two-component system, there was no loss of either parent or daughter isotope from either component, measurements on total rock samples of the sediment would result in a perfect isochron, the slope of which would correspond to the age of the original rock from which the sediment was derived. At the other extreme, if, during transport, all the daughter were lost, a perfect isochron would again result. This time the slope would correspond to the age of the consolidation. Neither of these two extreme cases resulting in collinear points in an isochron plot is likely to occur, but it is easy to show that, if one component loses no daughter, and the other component undergoes catastrophic loss of a fixed fraction of its daughter, the property of collinearity on an isochron plot is preserved. If the sediment is, as it should be, regarded as consisting of regions of different mixtures of the two basic components, collinearity is to be expected in an isochron, and the results reported by Compston and Pidgeon[25] and Whitney and Hurley[26] (which according to Allsopp and Kolbe[2] are "found to be surprisingly collinear") are, in fact, to be expected. The isochron slope, however, will not lead to an "age" that has any meaning. Although collinearity of the isochron points may be expected, the intercept of a false isochron line will indicate an abnormal value for the *ab initio* ^{87}Sr/^{86}Sr ratio. Where this conflicts with an experimental value measured on a parent-free component, it may be taken as an indication that the isochron is a misleading one. This appears to be the case for the Malmesbury sediments. The value of the ^{87}Sr/^{86}Sr ratio for the Piketberg limestone measured by Allsopp and Kolbe[2] is well below the "isochron" intercept on the ^{87}Sr/^{86}Sr axis.

Since there can be no knowledge of the changes in concentration of either parent or daughter in the erosion, transport and consolidation process of the sediments, the "age" derived from an "isochron" may be completely misleading. If the argument above about the collinear isochron and the dating of sediments is valid, the age of about 600 × 10^6 yr for the Malmesbury system would appear to be suspect. Jansen[23] concluded that the Bitterfontein paragneiss was derived from "Malmesbury system" sediments. Nicolaysen[27] found an age of 1050 × 10^6 yr for this paragneiss. The Malmesbury sediments, on this interpretation, would appear to predate the Cape Granite intrusion by a considerable period. If this is the case, the marked coincidence

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* The Rb–Sr isochron conventionally used is a plot of the ^{87}Sr/^{86}Sr ratio against ^{87}Rb/^{86}Sr ratio. A straight line plot results, with a slope corresponding to the age of the samples, and an intercept on the ^{87}Sr/^{86}Sr axis corresponding to the *ab initio* ratio.

of the ages of the granite and the granitized xenolith can only lead to the interpretation that the metamorphism was sufficiently intense to eliminate all previous "Malmesbury history" from the xenolith.

In this particular case the conclusion of an intense metamorphism is not surprising. The possibility exists that a scale of metamorphism, based on a measure of retention of pre-history, may be usefully developed. Argon retention is one obvious possible basis for such a scale, although it may be found that the sensitivity is too great, and that even mild metamorphic events are sufficient to eliminate all traces of the past. On the other hand, the recent work of Webb and McDougall[28] may indicate that, in some cases at least, a correlation between argon retention and extent of mineral alteration may be possible.

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Zusammenfassung—Kalium-Argon-Altersdaten des Gesamtgesteins sowie der leichten und schweren Mineralanteile des Kapgranits und eines granitisierten Xenoliths aus den Malmesbury-Ablagerungen werden mitgeteilt. Das Alter liegt zwischen 430 und 554 Millionen Jahren. Die schweren Mineralanteile zeigen jeweils das höchste Alter mit 540 (Granit) und 554 (Xenolith) Millionen Jahgren. Diese Alterswerte werden als untere Grenzen interpretiert; das Granitalter bestätigt die Angabe von 553 Millionen Jahren durch Rubidium-Strontium-Datierung. Die Übereinstimmung im Alter zwischen den verschiedenen Granit- und Xenolithfraktionen wird im Lichte der verschiedenen Hypothesen über das Alter der Malmesbury-Sedimente diskutiert. Es wird der Schluß gezogen, daß die Vorgeschichte vor der Granitisierung ausgelöscht ist. Als eventuelles Maß für metamorphe Aktivität wird die Argonretention vorgeschlagen.

Résumé—On rapporte les âges obtenus par datage potassium-argon pour la roche totale, la fraction minérale légère et les fractions minérales lourdes du granit du Cap et pour une xénolithe granitée provenant des sédiments de Malmesbury. Ces âges se situent entre 430 et 554 millions d'années. Les fractions minérales lourdes de chaque type de roche montrent le plus grand âge, 540 (granit) et 554 (xénolithe) millions d'années. Ces âges sont interprétés comme des limites inférieures, et l'âge du granit confirme l'âge de 553 millions d'années trouvé par datage rubidium-strontium. On discute de la coïncidence des âges des différentes fractions des échantillons de granit et xénolithe à la lumière des différentes suggestions sur l'âge des sédiments de Malmesbury. On arrive à la conclusion que toute l'histoire de pré-granitisation a été éliminée. On suggère la possibilité d'emploi de la rétention de l'argon comme mesure de l'activité métamorphique.

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OCCURRENCE OF BROMINE IN PLANTS AND SOIL

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Summary—The usefulness of X-ray fluorescence analysis for the determination of bromine in soil and plants is demonstrated by comparing the results with those obtained by activation analysis. An abnormal accumulation of bromine in some soils, plants and cigarettes has been found. Volcanic ash soil accumulates bromine in its humic acid. The large ratio of chlorine to bromine in river water may be explained by the accumulation of bromine in humus of soil. The possibility of bromine contamination of food and cigarettes, due to the application of agricultural chemicals, is pointed out.

ACCORDING to previous reports,[1,2] the level of bromine in the various materials of the lithosphere, hydrosphere and biosphere is, with a few exceptions, about 10 ppm as shown in Table I. There are few reliable determinations of bromine in soil and plant materials, but such measurements are of interest geochemically and of importance as a guide to contamination from the residues of agricultural chemicals. Recently, X-ray fluorescence analysis[3,4] and activation analysis[5–7] became available for the determination of bromine, and this report describes the determination of bromine in soils and plant materials by these methods.

EXPERIMENTAL

X-ray Fluorescence Analysis

Apparatus and experimental conditions

X-ray tube. Machlett OEG-50, tungsten target, voltage 30–40 kV, current 5–10 mA
High power unit. Rigaku Denki Model D-3F
Spectrometer. Rigaku Denki Goniometer K III
Detector. Scintillation counter with LiF crystal
Collimator. 0·15 × 100 mm
Pulse-height analyser. Set to 90% of bromine K_α counts
Counting strategy. Fixed counts, generally 10000
Chart speed. 1 cm/min
Time constant. 1 sec
Scanning speed. 1°/min

Procedure

Preparation of samples. Samples were always ground below 100-mesh size in order to obtain consistent and reproducible results. The K_α line of selenium was used as internal standard for quantitative analysis. A solution of sodium selenate was mixed well with the sample to make a homogeneous specimen containing 500 ppm of selenium.

Preparation of standards. Analytical reagent grade ammonium bromide (0·613 g) was dissolved in water and diluted to 1 l. to make a 500-ppm bromide solution. Definite amounts of this solution and the selenium solution were added to pure silicic acid or to starch washed with water, to make 10, 30, 50, 100, 200, 300, 500, 700 and 1000 ppm bromine standards for soils and plants respectively.

Qualitative analysis. The spectrometer was adjusted to the copper K_α line at 1·524 Å. About 1 g of sample was compacted in a plate mould and set on the sample holder, and the X-ray spectra were obtained under the conditions mentioned above.

Quantitative analysis. The spectrometer was set to the bromine $K\alpha$ line at 1·041 Å and selenium $K\alpha$ line at 1·106 Å, and the time for 10000 counts was measured. A calibration curve for the determination of bromine was made from the I_{Br}/I_{Se} intensity ratio and bromine content for standards. Bromine contents in samples were calculated from this curve.

Activation Analysis

As Menon[7] has pointed out that the non-destructive activation analysis of bromine in soil is sometimes interfered with by lanthanum, the destructive method of activation analysis was used in this work.

Apparatus

Reactor and irradiation. KUR Kyoto University Reactor (swimming-pool type 1 MW); 5×10^{12} n.cm^{-2}. sec^{-1}.

Gamma spectrometer. Hitachi RAH-403 400-channel analyser, with 3·5 × 2·5 cm sodium iodide crystal.

Procedure

About 0·1 g of dried sample was wrapped in polyethylene film for irradiation. A definite volume of ammonium bromide and ammonium chloride standard solution was taken and absorbed on filter paper (Toyo No. 5c, 2 × 2 cm) to make a standard containing 500 μg of chloride and 50 μg of bromide. The paper was dried under an infrared lamp and then wrapped with polyethylene film for irradiation. The samples and standards were irradiated with thermal neutrons for 30 min.

Carrier (sodium chloride, 100 mg) was added to the irradiated samples and standards which were then decomposed and distilled with a mixture of sulphuric and nitric acids. The distillates were absorbed in cooled 5*N* sodium hydroxide. The solution was made weakly acidic by addition of nitric acid to drive off the carbon dioxide. Silver bromide and chloride were co-precipitated from the solution by addition of excess of 0·1*M* silver nitrate. The precipitate was centrifuged and washed thoroughly twice with water, the washings being discarded. Then the precipitate was transferred to a weighed counting tray. It was dried under an infrared lamp and weighed to determine the chemical yield; activity of the 2·15 MeV gamma peak of ^{38}Cl was measured within 2 hr and that of the 0·550 MeV peak of ^{82}Br was measured after 10 or more hours of cooling. Radiochemical purity was confirmed by plotting decay curves and gamma spectra. The chlorine and bromine contents were calculated by the comparison of the radioactivities of the samples and standards after correction for chemicals yields and radioactive decay.

RESULTS

A few examples of the X-ray spectra of the different kinds of soils in Japan are shown in Fig. 1. The Isahaya and Futsukaichi soils are alluvial soil and the Saitobaru and Kawaminami soils are volcanic ash soil. The latter soils are rich in humus and distributed widely in Japan. As shown in Table I, 1–40 ppm of bromine in soils has been reported, but abnormally high bromine accumulation was found in humic volcanic ash soils.

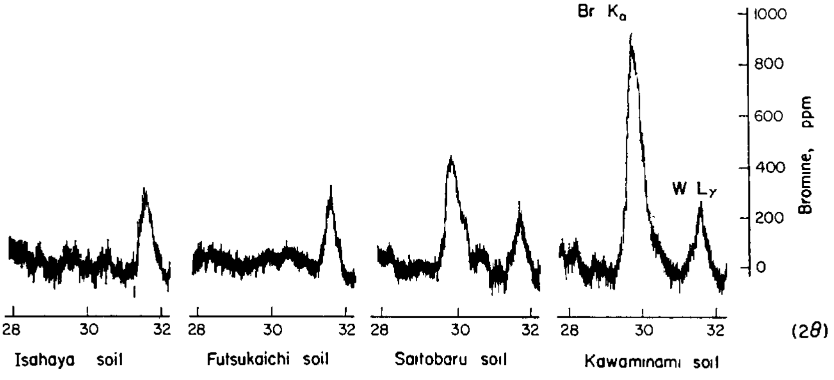

FIG. 1.—X-ray spectra of various soils.

TABLE I.—BROMINE CONTENTS (*ppm*) IN VARIOUS MATERIALS

Lithosphere	granite	2	biotite	5
	basalt	8	hornblende	10
	hypersthene	8	leucite	2
	labradorite	20	sodalite	2
	igneous rocks	1–9·4		mean 3·1
	sedimentary rocks	1–137		mean 3·9
Hydrosphere	river-water		0·0006	
	sea-water		65	
Biosphere	soils		1–40	
	marine muds		25–70	
	vegetables		0·5–20	
	cow's milk		0·18–0·21	
	human blood		3·6–5·8	

The bromine contents in soils sampled from different horizons at Kawaminami were determined by X-ray fluorescence and activation analysis. The results from the two methods were in good agreement, as shown in Table II. There appears to be a correlation between bromine and carbon levels in soil but none between chlorine and bromine.

TABLE II.—BROMINE, CHLORINE AND CARBON CONTENTS IN VARIOUS HORIZONS OF KAWAMINAMI SOIL

Horizon, *cm*	Carbon, % Tyurin method	Bromine, *ppm* X-ray fluorescence analysis	Bromine, *ppm* Activation analysis	Chlorine, *ppm* Activation analysis
0–15	5·60	269	261	123
15–35	2·14	127	132	339
35–65	17·4	848	852	468
65–90	1·59	106	113	368
90–	4·24	325	333	402

The correlation between carbon and bromine contents in many soils in Japan is shown in Fig. 2 together with a regression line for the data on the volcanic ash soils. A fairly high correlation was found among volcanic ash soils. The volcanic ash soils used as paddy fields contained rather low bromine levels. The low bromine content of non-volcanic ash soil is in agreement with previous reports. Peat soils had a high level of carbon, but a low level of bromine.

The X-ray spectra of Kawaminami soil untreated (1), and of the same soil washed with water (2), treated with 30% hydrogen peroxide (3), and washed with water after hydrogen peroxide treatment (4) are shown in Fig. 3. Bromine was not removed by washing with water, but decreased on washing with water after hydrogen peroxide treatment.

The X-ray spectra of the humus and humic acid obtained from the Kawaminami soil are shown in Fig. 4. The former was separated by the treatment of soil with 1*M* hydrofluoric and hydrochloric acids, and the latter was precipitated with sulphuric acid from a 0·25*M* sodium hydroxide extract of soil. As shown in Fig. 3 and Fig. 4, bromine was present mostly in the humus, especially in humic acid.

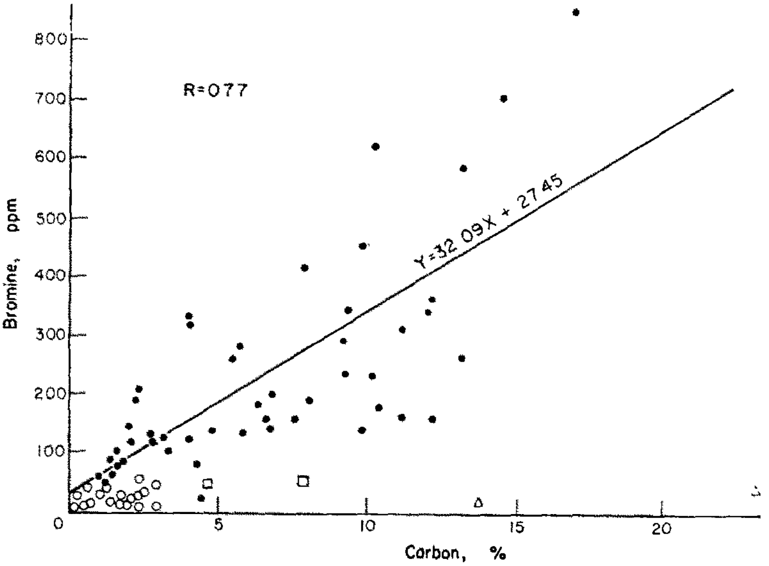

FIG. 2.—Correlation between bromine and carbon contents of soils. ●—Volcanic ash soil; □—volcanic ash soil used as paddy field; ○—non-volcanic ash soil; △—peat soil.

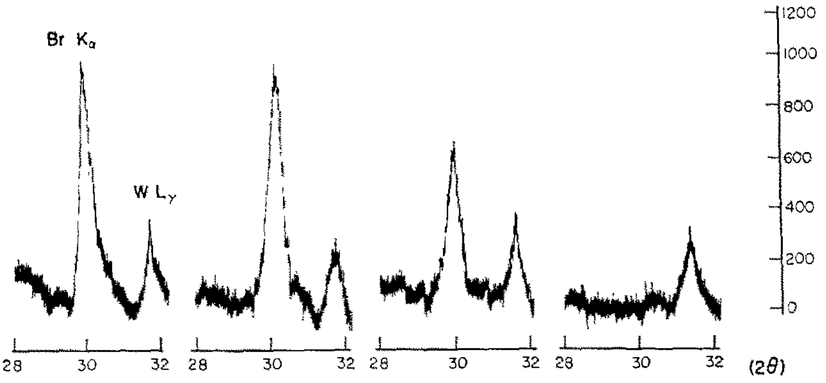

FIG. 3.—X-ray spectra of soil variously treated. (1) Untreated Kawaminami soil; (2) same soil washed with water; (3) same soil treated with H_2O_2; (4) same soil treated with H_2O_2 and then washed with water.

Table III shows the bromine contents of several kinds of plants. The bromine contents of most plants (except carrot treated with a nematocide containing bromine) are usually low and agree with the results in previous reports.

The bromine contents of tobacco plants cultivated in various parts of Japan are shown in Table IV. Some of these plants were cultivated on the humic volcanic ash soils with high bromine contents, but low bromine contents were found in all these samples. This result also agreed with previous reports. However, high bromine contents were found in all cigarettes, as shown in Table V.

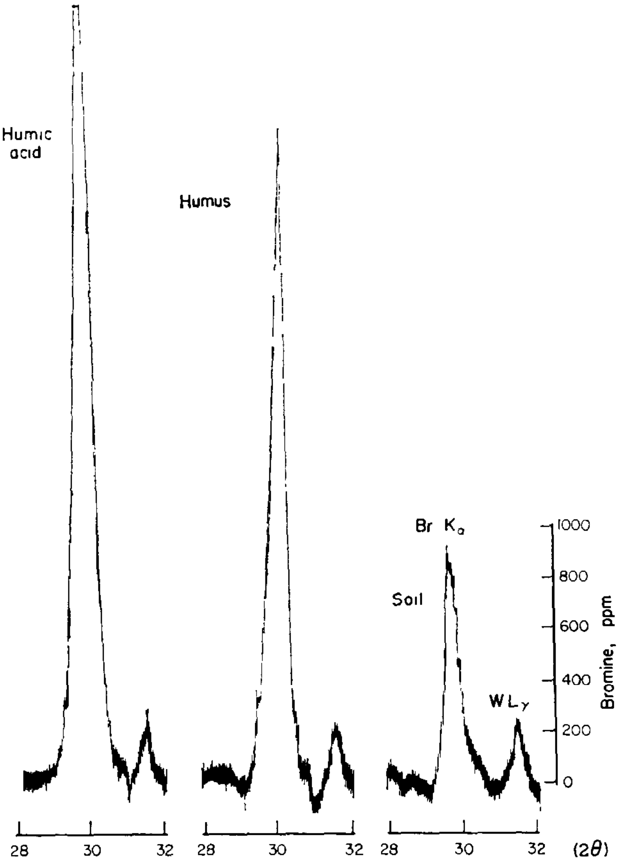

FIG. 4.—X-ray spectra of humus and humic acid from Kawaminami soil.

TABLE III.—BROMINE CONTENTS IN SEVERAL VEGETABLES*

Vegetable	Br, *ppm*	Vegetable	Br, *ppm*
carrot leaves†	615	sweet potato	10
carrot root	155	egg-plant	10
radish	20	cabbage	10
turnip	15	onion	34
potato	10	tomato	32

* Determined by X-ray fluorescence analysis.
† Treated with nematocide containing bromine.

TABLE IV.—BROMINE CONTENTS IN TOBACCO LEAVES FROM VARIOUS DISTRICTS IN JAPAN*

District	Br, *ppm*	District	Br, *ppm*
Fukuoka	28	Miyazaki	<10
Fukae	26	Osumi	17
Bungo Takada	10	Kobayashi	16
Nozu	17	Mikasa	<10
Ozu	24	Kokubu	<10
Kamimura	<10	Yamagawa	10
Kamitsuura	<10	Chiran	50

* Determined by X-ray fluorescence analysis.

Table V.—Bromine contents (*ppm*) in cigarettes, determined by X-ray fluorescence analysis

Name	I	II	Name	I	II
Rothman	450	—	Fuji	235	258
	(465)	—		(220)	—
Winston	84	—	Yamato	352	224
	(88)	—		(334)	—
555	140	—	Peace	298	204
Pall Mall	128	—	Izumi	200	195
Salem	100	—	Hi-lite(L)	162	186
Kool	91	—	Hope	168	177
Malboro	126	—	AAA	182	146
Viceroy	98	—	Shinsei	178	146
Ikoi	145	123	Wakaba	160	137
Kohaku	275	286	Hibiki	120	135
mf	312	262	Hi-lite(S)	166	138

I Obtained in market 9 September 1967.
II Obtained in market 17 October 1967.
( ) Determined by activation analysis.

DISCUSSION

The X-ray fluorescence analysis of bromine in soil and plant is simpler and easier than any other method. The accuracy of this method could not be assessed by means of the destructive conventional method, as bromine is highly volatile, but the bromine contents in soils were determined by X-ray fluorescence analysis and activation analysis, and the results agreed well.

An abnormal accumulation of bromine, 850 ppm, was found in humic volcanic ash soil. The bromine in this soil is supposed to be derived from sea water and brought by rain over a very long period, as the occurrence of bromine in most materials in the lithosphere and hydrosphere is about 10 ppm; the major exception is sea-water with 65 ppm. A fairly high correlation between carbon contents and bromine contents in volcanic ash soil was found. It was found that bromine occurs in the humic acid of soil. The mechanism of this bromine accumulation is geochemically important. From the data in previous reports,[2] the ratio of chlorine to bromine in rocks, sea-water and river-water can be calculated to be about 10–50, 300 and 1400 respectively. If the chlorine and bromine in river-water are derived from rocks and sea-water (*via* rain), the ratio of chlorine to bromine in river-water should be much smaller than it is. This suggests that chlorine and bromine in soil behave differently, and that bromine may be more active than chlorine in the biosphere. The accumulation of bromine in the humus of soil may explain the large river-water ratio.

The bromine content of plants, even those cultivated on volcanic ash soil with high bromine contents, is usually at the 10 ppm level, but Stelmach[8] and Brown[9] have shown that some crops contain bromine which may be derived from nematocides.

Tobacco plants contain the normal amount of bromine but considerably more is found in cigarettes, which may be contaminated by methyl bromide used as a fumigant during processing after harvest. It seems that the application of agricultural chemicals sometimes gives rise to accumulation of bromine in agricultural products. Further research on this problem is necessary from the hygienic point of view.

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Zusammenfassung—Der Nutzen der Röntgenfluoreszenzanalyse zur Bestimmung von Brom in Boden und Pflanzen wird durdh Vergleich der Ergebnisse mit denen der Aktivierungsanalyse demonstriert. Es wurde eine abnormale Anreicherung von Brom in einigen Böden, Pflanzen und Zigaretten gefunden. Vulkanischer Aschenboden reichert Brom in seiner Huminsäure an. Das große Chlor: Brom Verhält nis in Flußwasser kann durch die Anreicherung von Brom im Bodenhumus erklärt werden. Auf die Möglichkeit des Auftretens von Bromin Nahrungsmitteln und Zigaretten durch die Verwendung von Agrikulturchemikalien wird hingewiesen.

Résumé—On démontre l'utilité de l'analyse par fluorescence aux rayons X pour le dosage du brome dans le sol et les plantes en comparant les résultats à ceux obtenus par analyse par activation. On a trouvé une accumulation anormale de brome dans quelques sols, plantes et cigarettes. Le sol de cendres volcaniques accumule le brome dans son acide humique. On peut expliquer le rapport élevé du chlore au brome dans l'eau de rivière par l'accumulation du brome dans l'humus du sol. On fait ressortir la possibilité de contamination par le brome des aliments et cigarettes due à l'application de produits chimiques agricoles.

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PHOTON-ACTIVATION ANALYSIS FOR CARBON AND OXYGEN

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Summary—A method is described for the determination of carbon and oxygen in organic materials by means of the reactions $^{12}C(\gamma, n)^{11}C$ and $^{16}O(\gamma, n)^{15}O$. Samples are irradiated with bremsstrahlung from a 32-MeV electron beam impinging on a tungsten target, and the active products are separated before the positron annihilation gamma rays are counted. Limits of detection of 0·003 μg of carbon and 0·1 μg of oxygen are obtained.

THERE is considerable interest at the present time in the metallurgical properties of pure metals and ceramics, because it is only by having a thorough understanding of the causes of embrittlement that the properties of materials can be altered and fabrication costs reduced. It is generally accepted that non-metallic impurities such as carbon, nitrogen and oxygen, which occupy interstitial sites in the lattice, can have a marked influence on metallurgical properties even when only minute traces are present, and it has become necessary to devise very sensitive methods for their determination.

The standard method for the determination of carbon involves the combustion of the sample in pure oxygen, chemical processing to remove sulphur dioxide and water, and assay of the carbon dioxide in the gas stream by one of the following methods: gravimetry after absorption in soda-lime, manometry after freezing out in liquid oxygen, or conductimetry after absorption in barium hydroxide. In spite of meticulous precautions there is always a small variable blank due to carbon in the oxygen stream or the furnace boat, or diffusion through the walls of the apparatus. Furthermore it is impossible to guarantee that the specimen will remain uncontaminated during transfer into the furnace following preparation or cleaning.

Many materials, including high-alloy steels and ceramic materials, require a flux to assist in dissolution and oxidation and the flux will inevitably contribute to the blank.

Some of the limitations described above also apply to the standard method of measuring oxygen in metals by vacuum fusion or inert gas fusion. Oxygen is usually measured manometrically as carbon dioxide after oxidation of the carbon monoxide which is evolved from the sample in a graphite crucible at a high temperature. Small variable blanks from the apparatus and the flux again limit the ultimate usefulness of the method.

Activation analysis has the advantage that apparatus and reagent blanks are eliminated and offers the further advantage that a specimen can be cleaned or etched between irradiation and measurement, thus allowing the analyst to investigate the nature of the surface and whether or not it is typical of the bulk of the sample. Unfortunately, in this field, there are no suitable thermal neutron reactions and the only fast neutron reaction of value is $^{16}O(n, p)^{16}N(t_{\frac{1}{2}}\ 7{\cdot}35\ sec)$. This reaction has been used by many workers and is very useful for non-destructive determination of oxygen in many matrices. However, it is not particularly sensitive when currently available neutron sources are used, and the half-life of the product is inconveniently short.

The only other activating radiations which are sufficiently penetrating to be used on large samples are gamma photons, which will produce nuclear reactions of the type $^{A}Z(\gamma, n)^{A-1}Z$. An intense beam of gamma photons is required, having an energy in excess of the threshold energy of the required reaction. No known nuclear disintegration provides such energetic photons, but they can be produced by stopping charged particles of the required energy, a process known as "bremsstrahlung" production. The most efficient conversion of energy into bremsstrahlung radiation occurs when a light particle is stopped in a heavy absorber, and this is realized physically by causing a beam of energetic electrons from an accelerator to impinge on a target or "radiator" of platinum, gold or tungsten.

Several workers have reported the use of the reactions $^{12}C(\gamma, n)^{11}C(t_{\frac{1}{2}}\ 20{\cdot}3\ min)$ and $^{16}O(\gamma, n)^{15}O(t_{\frac{1}{2}}\ 2{\cdot}1\ min)$ for the determination of carbon and oxygen respectively by counting the sample after irradiation and resolving the decay curve into its components.[1–4] Engelmann[5] has given a detailed assessment of the value of varying the energy of the activating gamma rays. These methods are subject to interferences caused by activation of other impurities which give rise to short-lived positron emitting products such as nitrogen, copper, chlorine, or by activation of the matrix itself, *e.g.*, molybdenum, tungsten, iron.

These interferences can be eliminated by chemical separation of the required element and it is this particular aspect which is described in this paper.

A similar method for the determination of carbon in pure iron has recently been described by Revel *et al.*[6]

EXPERIMENTAL

The accelerator and photon irradiation facility

The electron linear accelerator at A.E.R.E. is an integral part of the neutron booster project and its principal function is to provide nanosecond pulses of electrons of up to 40 MeV energy. The electron beam normally terminates in a mercury target within the ^{235}U core of the booster but for the present work it is deflected by a d.c. magnet and emerges from the evacuated region of the accelerator through an air-cooled aluminium window. In order to minimize the possibility of a catastrophic fracture of this window the beam current is limited to 30 μA. The electron beam traverses a small air gap and impinges on a 3-mm thick tungsten target and the bremsstrahlung of photons is produced from this point. Behind the tungsten target is a device for the electrical monitoring of the beam current, and a void into which samples can be introduced by a pneumatic transfer system. The whole of the sample volume is permeated with gamma photons.

Samples can be loaded at any time, and the irradiation is carried out by energizing the deflecting magnet so that the electron beam falls on the target. It is usual to run the accelerator at 32 MeV with a current of 5–10 μA for a period of time roughly equal to one half-life of the isotope required. Immediately after the end of the irradiation the sample is recovered, placed in a lead carrying pot with remote-handling tongs, and transferred to the processing laboratory.

Most of the electron current in the accelerator is tightly focussed but there is of course a small spatial scatter. It is sensibly monoenergetic but owing to imperfections in design and adjustment, made worse by the use of relatively long pulses, there is a small energy spread, perhaps 10%. The beam which arrives at the irradiation position is not circular. In the vertical plane most of the current is confined to a beam about 2·5 mm thick, but in the horizontal plane a fan of energies is produced by the deflecting magnet, which also acts as an analysing magnet. The irradiation assembly is placed so that the tungsten radiator is symmetrical with respect to the beam and a narrow range of energy is converted into bremsstrahlung. The electron beam either side of the radiator falls on an aluminium block and is absorbed, with a comparatively small generation of bremsstrahlung. About one third of the electrons are stopped in the tungsten, the remainder being stopped in the current monitor before reaching the sample, and a bremsstrahlung beam is produced within a small solid angle in the forward direction.

Arrangement of samples in the photon flux

The distribution of the photon flux is far from homogeneous and shows evidence of the horizontal spread of the electron beam. However, if the samples are limited to dimensions of a few mm the flux varies by only 20% from one edge to the other. In the axial direction the flux diminishes with distance from the radiator and is attenuated by the material in the sample chamber.

An aluminium cylinder with a recess drilled into it is used as a sample holder. It has been found convenient to use samples 6 mm in diameter with thin standards of the same size placed either side. If more than one sample is to be irradiated then standards are placed between each sample and at the front and back of the whole assembly. Larger and irregular samples can also be accommodated but the best arrangement of sample and standards in the beam must be decided for each specimen. For calculation of results the sample is compared with the standards between which it was sandwiched. These may differ in specific activity by up to 20%, depending on the thickness of the sample, and a mean specific activity is taken. In the case of thick samples of high atomic number the attenuation may be as much as 40% and a geometric mean activity would be more applicable.

Sample preparation

Samples should either be machined to the correct size or fabricated from powder or turnings by compression in a die. In either case precautions must be taken against contamination. After shaping, the samples are handled only with stainless steel forceps in clean surroundings. When carbon is to be determined, paper, plastic, grease, oils, and alkalis which can absorb dioxide from the air must be carefully excluded. The samples are washed first in acid, then in water, degreased in ether and thoroughly air-dired. They are then individually wrapped in small pieces of aluminium foil, which have been degreased in ether, before loading into the sample holder. The standards are also wrapped in thin aluminium foil to avoid small fragments of the standard contaminating the interior of the sample holder.

Radiochemistry

In spite of careful handling there is always the possibility of external contamination. In the case of materials such as ceramic calcium oxide it is certain that the surface will have absorbed atmospheric carbon dioxide and it would be desirable to remove this layer before analysis. Samples are therefore washed or etched and then re-weighed. The weight loss due to this operation is usually only a few mg and the operation can be carried out in a few min, certainly in a time which is short compared with the half-life of ^{11}C, 20·3 min.

Samples for oxygen determination are etched in acid, in such a way as to remove a reasonable amount from the surface in a few seconds only.

Separation of carbon

Certainly the quickest and best documented method for the removal of carbon from materials in which it may be present as free carbon, carbides, carbonates, organic compounds *etc.*, is total combustion in a stream of oxygen, if necessary with a suitable flux. This technique was chosen in this work and the precise experimental details are given below. All that is required of the separation procedure is that it should extract 100% of the carbon in the sample, a criterion with which one is familiar in methods of carbon analysis. Unlike conventional techniques the method of gamma activation analysis does not require that any flux which is used should have a low and reproducible carbon content.

Combustion apparatus. The apparatus used for the combustion of samples and the subsequent purification and recovery of the carbon is shown in Fig. 1. Furnace **A** with alumina tube **B** can be operated at temperatures up to 1450°. The sample is placed in a combustion boat **C** which is introduced *via* the removable silica window **D** and pushed into the hot zone by means of a stainless-steel rod. Oxygen gas is introduced through a side-arm, and the pressure is regulated by the level of water in the bubbler **E**. A silica wool plug serves to remove particulate matter from the gas stream, which is then passed through manganese dioxide and magnesium perchlorate at **F** and **G** to remove sulphur dioxide and water. The gas stream then passes through a flow-meter **H** and finally through a solid absorption tube **J** or the multi-loop trap **K** which can be cooled in liquid oxygen, before being vented to the atmosphere. The remainder of the apparatus is concerned with the measurement of the pressure of carbon dioxide and transfer of the gas to the counting vessel **L**.

Steels. For the combustion of steels the sample is placed in a fireclay boat which is slid into the

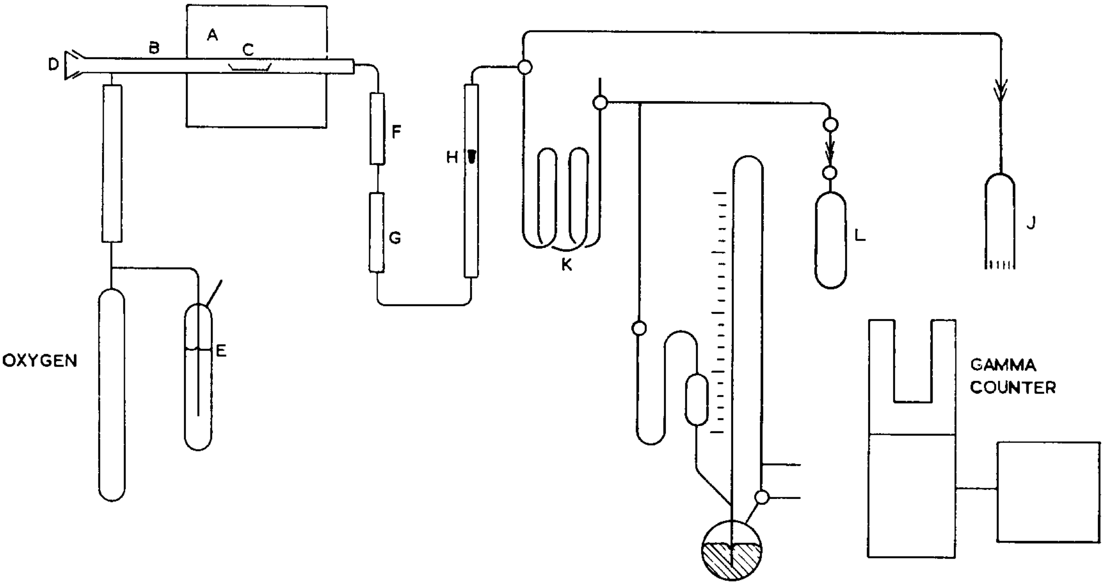

FIG. 1.—Apparatus for the separation, collection and measurement of radio-carbon.

hot zone of the furnace tube and observed through the silica window. The time is recorded at which combustion is complete. The furnace temperature is chosen so that combustion is complete in about 2 min, 1150° for low-alloy steels and up to 1350° for stainless steels. The oxygen flow-rate is 400 ml/min and the apparatus is purged for 4 min after the end of combustion to ensure collection of all the evolved carbon dioxide. A hot copper oxide furnace to complete the oxidation of carbon monoxide to dioxide was found to be unnecessary. A flux or accelerator is not normally required although certain steels become protected by a thin oxide layer which prevents complete combustion, and in these cases a little tin metal, or a few turnings of a mild or low-alloy steel can be added to the boat to assist combustion.

Molybdenum. The combustion of molybdenum requires different conditions. A temperature of 1250° is used, and because of the volatility of the oxide it is necessary to take care to keep the furnace tube clear of any molybdenum trioxide which has condensed in the cooler regions. A flux is unnecessary and may even be a disadvantage. (Molybdenum is more dense than tin or iron and has been observed to sink into and be covered with these flux media so that it is incompletely burned.)

Magnesium oxide. Carbon in magnesium oxide could be present as free carbon, carbide, or carbonate, and its complete removal would require the sample to be dissolved at high temperature in an oxidising environment. A large platinum boat is used which contains 3 g of ground fused borax. The crudely broken up sample of magnesium oxide is scattered on the borax and the boat slid into the hot zone of the tube. It was found to be necessary to control the temperature at 1250 ± 20°. Below this temperature the rate of dissolution is too slow for convenience, whereas at higher temperatures there is significant volatilization of the borax, which is then found to be distributed throughout the hot zone of the furnace, making it difficult to remove the platinum boats and considerably shortening the life of the furnace tube. Under the conditions outlined complete dissolution of the ceramic is achieved in 4 min and a further 2-min purging of the apparatus serves to transfer all the evolved carbon dioxide to the trap. This method of dissolution has been applied to ceramic calcium oxide and ceramic alumina and would appear to be quite generally applicable to such ceramics.

Separation of oxygen

Oxygen is extracted from irradiated metal samples by fusion in a graphite crucible in an atmosphere of argon. A small quantity of tin or iron is used as a flux. By contrast to the normal practice of inert gas fusion it is not necessary to outgas the furnace or to use a flux which is low in oxygen content.

The fusion apparatus. A conventional inert gas fusion apparatus was used. Argon, which need not be specially purified, is fed through a flow-meter into a silica furnace assembly. The gases leaving the furnace pass over hot copper oxide, then iodine pentoxide which ensures complete oxidation of carbon monoxide and then through "carbest" which retains carbon dioxide. The furnace consists of a graphite crucible heated to 2000° by an induction heater. Samples are introduced after irradiation and fused with a suitable flux for 2 min while the argon is flowing through at a rate of 200 ml/min. The carbest tube is then removed and transferred to the counter.

Standards

The provision of accurate and reliable standards is essential for any analytical method. A satisfactory standard for this work must have an accurately known content of the element to be determined; it should also be the same size and shape as the sample, self-supporting and strong enough to be wrapped in aluminium foil without breaking. The particular circumstances of the gamma irradiation also require that the material should be chemically stable and infusible up to at least 150°.

Steel turnings are available, the carbon content of which is known with some certainty, and these can be pelleted very satisfactorily at pressures of up to 60 kg/mm^2. The pellets can then be weighed and the carbon content calculated. Alternatively, since the apparatus is set up for gas handling and manometry, the carbon content can be measured during the processing. This has the advantage of being an absolute measurement of carbon in the standard and allows the use of steels of unknown carbon content and even of pellets or punchings of unknown weight as standards. However the method is tedious and time-consuming.

A wide variety of organic polymers of known carbon content is available, and they can be punched out into disks for use as standards. Thin films from 0·025 to 0·25 mm thick were used in order to limit the amount of carbon to a few tens of mg so that the activities were not excessive. None of the materials tried was satisfactory. The specific activities induced were always low and variable compared with carbon steels and pure graphite. This effect may be due to a loss of active carbon from the material during the irradiation, possibly due to the large recoil energy which would break the chemical bonds and allow the active carbon atoms to form volatile molecules. The recoil distance for ^{11}C in organic polymers is too small to account for the loss directly.

The most satisfactory standard is pure graphite, pelleted into thin disks. Special grades of pelleting graphite are available (*e.g.*, Ringsdorff RWA) and as little as 10 mg can be formed into a disk 6 mm in diameter, which is sufficiently robust for the purpose. These standards can be weighed on an analytical balance to the necessary precision, and can be counted either unprocessed, in which case a small factor must be applied to normalize the counting geometry, or after processing and absorption of the carbon dioxide on carbest. It is usual to process and count all the samples first, and then to count the standards perhaps 1–2 hr after irradiation. The activities are still adequate after 3–6 half-lives and the half-life is known with sufficient precision for decay corrections to be made.

Reagent-grade boric acid can be pressed into 6 mm disks in a steel die to form satisfactory standards for oxygen; they can be made with a weight of 10 mg or less and contain 78% oxygen by weight. The decay curve of the standards can be resolved into three components, a 2-min half-life (^{15}O), a 10-min half-life [due to the reaction $^{16}O(\gamma, t)\,^{13}N$] and a 20-min half-life [$^{16}O(\gamma, n\alpha)^{11}C$]

Counting

^{11}C and ^{15}O decay by positron emission. There are no gamma rays. The most convenient method of counting is to detect the pair of spatially opposed coincident gamma rays which result from the annihilation of a positron with an electron. These 0·51-MeV gamma rays are counted with an NaI(Tl) crystal but a wide variety of counting geometries and pulse detection systems is available.

There are many reports in the literature, of coincidence counters being used for positrons. They have two very important advantages; first they are specific for gamma sources which give pairs of coincident gamma rays which are spatially opposed, and secondly, because of this, the background count-rates can be very low. A gain in specificity can also be achieved by using pulse-height analysis to restrict the counter response to a region around 0·51 MeV. Some workers have used a combination of both of these methods, but in this work the activities present in the source are known and these counting systems may be forfeiting sensitivity for the sake of specificity which is not required. The real criterion should be the limit of detection, which is governed by the "figure of merit", $E/\sqrt{B}$ where E is the counting efficiency and B is the background.

Various detector arrangements were tested for counting efficiency and background, *e.g.*, large and small crystals, well-crystals, a single-channel analyser and a γ–γ coincidence counter. The best performance was obtained with a 38 × 38 mm well-crystal used as a gross gamma-counter and this arrangement was adopted for all counting.

Scaling and timing

A counting assembly has been developed which comprises four 38 × 38 mm well-type NaI scintillators, each in its own castle and with its Harwell 2000 series electronics. Type 2179 scintillation adaptors feed type 2113 access scalers which are interrogated *via* a type 2223 paper tape controller. At the end of each counting period, for example 20, 40, 100 or 200 sec, the readout cycle is initiated, and clock time, counting period, and the counts recorded by each scaler are punched on 8-hole paper tape. The scalers are automatically reset and the operation is repeated. The four samples or standards are counted simultaneously with very little loss of data from the short-lived components of the decay. The paper tape is fed into an IBM 360/65 computer and the data reduced to the initial count-rates of the specified components of each decay curve.

Calculation

The mean specific activity induced in the sample is the arithmetic mean of the specific activities in the two standards immediately adjacent to it.

The specific activity is given by

$$A = \tfrac{1}{2}(C_1/W_1 + C_2/W_2)$$

and the concentration of the element being determined is

$$C_s/A \times W_s$$

where C is the normalized count-rate from the computer program, W is the weight, and the subscripts 1, 2 and s refer to the two standards and the sample respectively.

DISCUSSION

Radiochemical yield of carbon

It is assumed that the radiochemical yield of active carbon is 100%, *i.e.*, the active carbon present in the sample after irradiation is quantitatively transferred to the counting vessel. There is no doubt that this is the case for carbon in steels when the evolved carbon dioxide is collected in a multi-loop trap cooled in liquid oxygen.

This is the standard method used today for carbon in steel and the present apparatus used with a manometric finish gave results for B.C.S. steels in excellent agreement with the published figures. There can be little doubt also that carbon is completely released from molybdenum and other materials which form volatile oxides on burning in oxygen. In the case of ceramic materials, there is no reason to doubt that the carbon is completely released as carbon dioxide or monoxide provided that the sample forms a homogeneous melt with the flux. This is achieved under the conditions specified. Good yields were obtained from crystalline calcite (see Table I).

TABLE I.—RECOVERY OF CO_2 FROM CALCITE IN A BORAX FLUX

Calcite, *mg*	Carbon found, *mg*	Recovery, %
4·2	0·52	102
1·6	0·20	105
19·6	2·37	101
5·7	0·69	101·5
0·8	0·13	135

There was a small variable apparatus blank which has not been subtracted.

In the present work carbon dioxide is absorbed directly on carbest. The radiochemical recovery of this method has been checked by measurements on analysed samples and also by counting the same sample in the gas phase and absorbed on carbest. Samples of active carbon dioxide were put into the glass counting vessel and counted, and then transferred back into the multi-loop trap. The glass counting vessel was then replaced by a carbest tube. The carbon dioxide was allowed to sublime and was carried through the system by a stream of argon into the carbest which was then transferred to a glass counting vessel and counted in the well-crystal. After allowance for the slight change in counting geometry and the decay, the observed activities were always identical.

Radiochemical yield of oxygen

It is very difficult to establish beyond any doubt that the yield of oxygen is 100%, but the method is likely to be as good as or better than inert gas fusion used in a conventional way with a manometric finish. There are two features of the method which give a distinct advantage. First it is not affected by blanks and therefore a flux can be used which contains oxygen to act as a carrier, and secondly there is no reason why the furnace should not be operated at extremely high temperatures with consequent serious outgassing which is normally unacceptable.

Radiochemical purity of sources

The radiochemical purity of carbon is established by examining the decay curve. Sources are also checked by gamma spectrometry and shown to emit only positron annihilation radiation at 0·51 MeV. Although this is not exclusive proof of radiochemical identity it is unlikely that any significant quantity of another nuclide is present.

Sources of oxygen activity are rarely pure, and a longer-lived component (usually ^{11}C) appears after several half-lives decay. The data are always analysed on a computer to give a best least-squares fit for two components with half-lives 2·1 min and 20·3 min.

Interferences

The radioactivity which is finally counted should be due only to a particular nuclide in an amount proportional to the concentration of impurity present. It is possible that the final source can contain the correct nuclide derived by an incorrect route, or the wrong nuclide. Both of these situations are described as interferences, the former nuclear, the latter chemical.

Nuclear interferences. It is convenient to illustrate nuclear interference with respect to carbon. The method relies on the nuclear reaction ^{12}C(γ, n)^{11}C but the same active product can be obtained in other ways, for example, ^{16}O(γ, αn)^{11}C, ^{11}B(p, n)^{11}C, ^{10}B(p, γ)^{11}C, ^{14}N(p, α)^{11}C.

The proton reactions can only occur as secondary reactions and are unlikely to become significant even in a matrix rich in boron or nitrogen; they can therefore be ignored. The (γ, nα) reaction is much more important and is a serious interference in oxygen-rich materials.

The cross-sections for the gamma reactions are energy-dependent, the reaction ^{12}C(γ, n)^{11}C having a threshold at 18·7 MeV and a peak at about 21·5 MeV, whereas the interfering reaction ^{16}O(γ, nα)^{11}C has a threshold of 25·8 MeV and the cross-section is comparable to that of the (γ, n) reaction at 30 MeV. This interference can be eliminated by reducing the energy of the beam below the threshold for the (γ, nα) reaction, but this affects the sensitivity of the determination, as the following considerations will show.

Cross-sections cannot be considered in isolation but must be compared with the gamma-photon energy spectrum of the bremsstrahlung. The degree of activation induced will be a function of the product of elements of flux and cross-section integrated over the range of energies from the threshold to the maximum energy of the electron beam, and the value of this function increases rapidly with electron energy. Some experimental data have been reported by Engelmann.[3,5,7] The activation will also be proportional to the mean current in the electron beam, which diminishes with increasing energy.

The selection of electron beam energy must therefore be a compromise among the conflicting requirements of overlap of cross-section and bremsstrahlung energy spectrum, current in the electron beam, and elimination of interferences. Whenever possible an energy of 32 MeV is used to achieve the maximum sensitivity but under these conditions a ceramic material which contains 40% of oxygen will appear to contain 0·2% of carbon by virtue of the (γ, nα) interference. The interference is eliminated by reducing the energy of the electron beam to 25 MeV but there is a tenfold loss in sensitivity.

Chemical interference. In spite of the fact that in most cases the decay curve of a source prepared from an analysis for carbon showed the half-life to be 20·3 min, there is always the possibility that some unsuspected nuclide has contaminated the final source. For this reason all possible nuclides were considered and purification steps included to remove them. Only volatile elements or compounds need be considered, because there are sufficient filters in the form of silica wool and solid reagents to remove particulate matter. ^{15}O will be diluted by the oxygen and is vented to the atmosphere. In any case the half-life is so short that no significant activity will remain at the time of counting. Water is removed on the desiccant, and sulphur compounds are removed on the manganese dioxide. The only activity which has been observed as a contaminant is ^{18}F, which arose from a sample of teflon. Normally small quantities of fluorine would react with the walls of the hot alumina furnace tube, but if this proves inadequate a furnace packed with alumina or magnesia removes fluorine compounds satisfactorily.

In the case of oxygen the sources are not pure and a 2-min half-life ^{15}O component is resolved from the decay curve. The only interferences will be due to other isotopes having half-lives very close to 2 min; ^{30}P($t_{\frac{1}{2}}$ 2·6 min) is the only one which need be considered, but any elemental phosphorus formed in the graphite furnace will not pass through hot copper oxide.

CONCLUSIONS

It is difficult to prove that a new analytical method gives correct figures because there is inevitably a shortage of analysed material at a suitable concentration level. This is particularly true in the case of oxygen as a trace impurity but it is safe to assume that B.C.S. steels have carbon contents which are known with certainty. Table II shows that the method gives excellent agreement with certificate figures over a wide range of concentration. At lower levels replicate analyses on samples of zone-refined molybdenum are very reassuring (Table III).

The ultimate sensitivity of the method is determined by the minimum quantity of radioactive product which can be detected, and this in turn is related to the efficiency

TABLE II.—THE DETERMINATION OF CARBON IN B.C.S. STEELS

B.C.S. steel	Certificate value, %	Gamma activation values, %
291	0·47	0·46
265	0·047	0·043, 0·048, 0·048, 0·047
292	0·070	0·068, 0·067
218/2	0·160	0·152
241/1	0·85	0·85, 0·87

TABLE III.—THE DETERMINATION OF CARBON IN HIGH PURITY MOLYBDENUM

Sample	Found, *ppm*
E	$0{\cdot}5 \pm 0{\cdot}05$, $0{\cdot}4 \pm 0{\cdot}05$
M	$0{\cdot}6 \pm 0{\cdot}1$, $0{\cdot}5 \pm 0{\cdot}05$
H	$0{\cdot}4 \pm 0{\cdot}1$, $0{\cdot}25 \pm 0{\cdot}1$

The error figures are based on the standard deviation of the counting statistics.

and background count-rate of the detector and to the specific activity of the required element at the time of counting.

In the case of carbon, the specific activity is 2000 c/min/μg 10 min after the end of the irradiation and the counter background is 140 c/min. If counting proceeds for one half-life and the background is known with great certainty, then twice the standard deviation of the background count can be shown to correspond to 0·003 μg of carbon. In the case of oxygen the 10-min delay before counting is a more severe penalty and the specific activity is usually 300 c/min/μg. The limit of detection is therefore about 0·1 μg.

The method can be applied to the determination of carbon and oxygen with great specificity and sensitivity in almost any inorganic substance. A limit of detection of less than 1 ppm can be achieved on samples of only 100 mg and it is possible to etch or abrade the surface of the sample, to eliminate surface effects, between irradiation and counting.

Zusammenfassung—Ein Verfahren zur Bestimmung von Kohlenstoff und Sauerstoff in anorganischem Material mit Hilfe der Reaktionen $^{12}C(\gamma, n)^{11}C$ und $^{16}O(\gamma, n)^{15}O$ wird beschrieben. Die Proben werden mit Bremstrahlung von einem auf ein Wolframtarget fallenden 32 MeV-Elektronenstrahl bestrahlt und die aktiven Produkte abgetrennt, ehe die gammaquanten aus der Positronenzerstrahlung gezählt werden. Man erhält Nachweisgrenzen von 0,003 μg Kohlenstoff und 0,1 μg Sauerstoff.

Résumé—On décrit une méthode pour la détermination du carbone et de l'oxygène dans des substances inorganiques au moyen des réactions $^{12}C(\gamma, n)^{11}C$ et $^{16}O(\gamma, n)^{15}O$. Les échantillons sont irradiés avec le "bremsstrahlung" d'un faisceau d'électrons de 32 MeV frappant sur une cible en tungstène, et l'on sépare les produits actifs avant de compter les rayons gamma d'annihilation de positron. On obtient des limites de détection de 0,003 μg de carbone et 0,1 μg d'oxygène.

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USE OF NEUTRON-ENERGY MODERATION FOR RESOLVING INTERFERENCES IN FAST-NEUTRON ACTIVATION ANALYSIS

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Summary—Four elements, vanadium, chromium, manganese and iron, have been determined in nickel-base samples after measurement of the intensity of two γ-lines; the 0·85-MeV γ-ray emitted by ^{56}Mn (produced from both Mn and Fe), and the 1·44-MeV γ-ray from ^{52}V (arising from V and Cr). The two elements contributing to each γ-peak were assayed separately from data obtained by irradiating each sample twice with neutrons of different energy distributions.

ACCELERATOR neutron sources have found application in neutron-activation analysis either when nuclear reactors have been inaccessible, or when fission neutrons have been incapable of inducing suitable nuclear reactions in the element to be determined. In particular, neutron generators producing 14-MeV neutrons by the reaction

$$ {}^{3}\mathrm{H} + {}^{2}\mathrm{H} \rightarrow {}^{4}\mathrm{He} + {}^{1}\mathrm{n} + 17{\cdot}6\ \mathrm{MeV} \qquad (1)$$

have received considerable attention, as high neutron outputs can be obtained at relatively low accelerating voltages of 100–150 kV. Highly endoergic reactions can take place with 14-MeV neutrons and a number have proved to be of considerable analytical importance (*e.g.*, ^{16}O(n, p)^{16}N) but nuclear interferences frequently occur between near-neighbours in the periodic table as the same radionuclide may be formed from more than one target element. These nuclear interferences often impose major limitation on the usefulness of fast-neutron activation analysis, particularly when the interfering elements cannot be determined separately and in certain cases only the sum of the required activity and that from interferences can be assayed.

Fast neutrons from a neutron generator employing the D–T reaction [equation (1)], together with the slow neutron component formed by moderation of the fast flux in the generator and surrounding materials, may induce (n, p), (n, α), (n, 2n), (n, n′) and (n, γ) reactions. Thus the nuclide ${}_{\mathrm{Z}}{}^{\mathrm{A}}\mathrm{M}$, where A represents mass number and Z the nuclear charge, may be formed by the following routes:

$${}^{\mathrm{A+1}}_{\mathrm{Z}}\mathrm{M}(\mathrm{n}, 2\mathrm{n})\,{}_{\mathrm{Z}}{}^{\mathrm{A}}\mathrm{M} \qquad (2)$$

$${}^{\mathrm{A-1}}_{\mathrm{Z}}\mathrm{M}(\mathrm{n}, \gamma)\,{}_{\mathrm{Z}}{}^{\mathrm{A}}\mathrm{M} \qquad (3)$$

$${}_{\mathrm{Z}}{}^{\mathrm{A}}\mathrm{M}(\mathrm{n}, \mathrm{n}')\,{}_{\mathrm{Z}}{}^{\mathrm{A}}\mathrm{M} \qquad (4)$$

$${}^{\mathrm{A}}_{\mathrm{Z+1}}\mathrm{N}(\mathrm{n}, \mathrm{p})\,{}_{\mathrm{Z}}{}^{\mathrm{A}}\mathrm{M} \qquad (5)$$

$${}^{\mathrm{A+3}}_{\mathrm{Z+2}}\mathrm{O}(\mathrm{n}, \alpha)\,{}_{\mathrm{Z}}{}^{\mathrm{A}}\mathrm{M} \qquad (6)$$

There is no change of atomic number in reactions (2), (3) and (4) and therefore these reactions will all serve to reinforce the contribution of ${}_{\mathrm{Z}}{}^{\mathrm{A}}\mathrm{M}$ formed from element

M. Consequently ${}_Z{}^AM$ may be produced from three source elements M, N and O and the intensity of the characteristic radiation from ${}_Z{}^AM$ will thus be made up of contributions from all three if these are present in the sample in appreciable quantities. This may be written

$$C_T = S_M W_M + S_N W_N + S_O W_O \tag{7}$$

where C_T is the total count of the radiation from ${}_Z{}^AM$ (say measured over a γ-ray peak), S_X is the specific activity of the sample derived from element X in counts/g under a given set of irradiation and counting conditions and W_X is the weight of element X in the sample. The mode of decay of the radionuclide ${}_Z{}^AM$ is independent of its method of formation and therefore provides no means of assessing the proportion of the yields derived from different target nuclei, but the specific activity S_X is not only characteristic of element X but is also a function of neutron energy. It has already been shown[1] that if the neutron energy is chosen carefully from a knowledge of reaction thresholds and Coulomb-barrier restrictions, interferences in fast-neutron activation analysis can be substantially reduced. An accelerator capable of functioning as a versatile neutron source and producing neutrons of various preselected energies must necessarily be more complex and expensive than a simple 14-MeV neutron generator, but an alternative method of obtaining neutrons with an energy of less than 14 MeV would be to reduce the energy of the neutrons from the generator by moderation. Neutrons with more than one energy distribution could therefore be used to irradiate the sample and equation (7) would then be rewritten

$$C_T{}^A = S_M{}^A\, W_M + S_N{}^A\, W_N + S_O{}^A\, W_O \tag{7A}$$

where the superscript A is used to distinguish the different conditions available for irradiation of the sample.

Thus three irradiations at different neutron energies would yield data for three simultaneous equations of the form of equation (7A) which could be solved for W_M, W_N and W_O once values for the specific activity constants had been found from standards. For solution of these equations it is clearly important that the product $S_X W_X$ should be significant when compared with C_T in at least one of the equations for each element.

A multiple irradiation procedure will clearly take longer to complete than activation analysis involving a single irradiation and counting cycle but the time penalty may not be severe if the additional irradiation and counting periods are kept short and provide extra useful information. Insertion of moderator between neutron-emitting target and sample will reduce the flux through the sample but in certain cases the relative changes in specific activity which occur in moving the sample to the lower flux positions may reduce masking of small quantities of activity from one element by large quantities from another.

As an example of the application of the technique we describe here the determination of four elements, vanadium, chromium, manganese and iron, in nickel-base samples by measurement of the yields of two radionuclides manganese-56 and vanadium-52.

EXPERIMENTAL

Neutron generator. The installation used in this work was based on a sealed-tube unit with a maximum neutron output of 10^{10} n/sec total (Elliott Electronic Tubes Ltd.). The system, which has been described in detail elsewhere,[8] was capable of controlling irradiation, cooling and counting times, flux monitor operation *etc.*

Preparation for irradiation

Samples were in the form of powder or turnings and were always pressed into cylinders with a 30-ton hydraulic press before irradiation, to ensure constant geometry and to avoid errors due to compacting during transfer. Dies were manufactured so that the pressed samples were of the correct diameter to fit into the standard polyethylene capsules used with the generator; the thickness of the compacted samples was controlled by pressing a measured weight of material.

Standards were made up to have a composition which was as similar to that of the samples as possible. Known quantities of the elements to be determined were added to nickel powder and carefully agitated in a special mixer before pressing.

γ-Ray spectroscopy. A 3 × 3 in. thallium-activated sodium iodide scintillator was used in conjunction with a 512-channel pulse-height analyser for γ-ray spectrometry. Data manipulation and calculation was carried out in a laboratory data processor.

RESULTS AND DISCUSSION

The products of the (n, p), (n, α), (n, 2n) and (n, γ) reactions with the most abundant isotopes of vanadium, chromium, manganese and iron are shown in Table I together with cross-sections for the production of the isotopes and the half-lives and γ-ray energies of the products. The cross-sections for the (n, p), (n, α) and (n, 2n) reactions are for neutrons with an energy of $E_n = 14$ MeV;[3] capture cross-sections apply to thermal neutrons.

The difficulty of determining the elements listed in Table I in the presence of each other is immediately apparent. Chromium can be determined by the reaction ^{52}Cr(n, p)^{52}V but vanadium and manganese interfere by the (n, γ) and (n, α) reactions respectively, while the (n, γ) reaction on manganese interferes with the determination of iron by the (n, p) reaction. The reactions of cobalt are not included in Table I as the quantity of this element in the samples was known to be below the level that could be detected with the neutron generator, but at higher concentrations the presence of cobalt would interfere with iron and manganese determinations by the production of ^{56}Mn by the reaction ^{59}Co(n, α)^{56}Mn.

Vanadium in the sample could be separately assayed from the intensity of the 0·32-MeV ^{51}Ti peak provided that the yield of low-energy γ-rays and Compton background was not high in the same region of the γ-spectrum, but for samples with high chromium content, allowance would be necessary for the 0·32-MeV contribution

TABLE I.—REACTIONS OF GENERATOR NEUTRONS WITH MOST ABUNDANT ISOTOPES OF VANADIUM, CHROMIUM, MANGANESE AND IRON

Element	Abundance, %	Reaction	Cross-section, *mbarns*	Half-life of product	$E\gamma$ of product, *MeV*
Vanadium	99·76	^{51}V(n, p)^{51}Ti	27·0	5·8 min	0·32
		^{51}V(n, α)^{48}Sc	28·6	44 hr	0·99
		^{51}V(n, 2n)^{50}V	—	Long	—
		^{51}V(n, γ)^{52}V	4500	3·76 min	1·44
Chromium	83·76	^{52}Cr(n, p)^{52}V	78	3·76 min	1·44
		^{52}Cr(n, α)^{49}Ti	—	Stable	—
		^{52}Cr(n, 2n)^{51}Cr	285	27·8 d	0·32
		^{52}Cr(n, γ)^{53}Cr	—	Stable	—
Manganese	100·0	^{55}Mn(n, p)^{55}Cr	75	3·5 min	no γ
		^{55}Mn(n, α)^{52}V	30	3·76 min	1·44
		^{55}Mn(n, 2n)^{54}Mn	825	303 d	0·84
		^{55}Mn(n, γ)^{56}Mn	13,300	2·56 hr	0·85, 1·81, 2·1
Iron	91·68	^{56}Fe(n, p)^{56}Mn	103	2·56 hr	0·85, 1·81, 2·1
		^{56}Fe(n, α)^{53}Cr	—	Stable	—
		^{56}Fe(n, 2n)^{55}Fe	500	2·7 yr	no γ
		^{56}Fe(n, γ)^{57}Fe	—	Stable	—

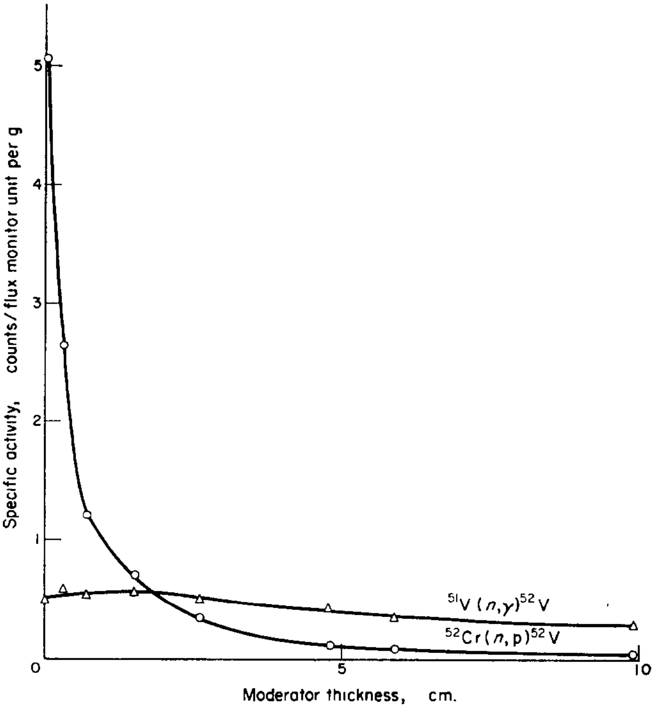

FIG. 1. Relative variation of neutron flux with distance from neutron-emitting target.

of ^{51}Cr produced by the reaction $^{52}Cr(n, 2n)^{51}Cr$. However, the multiple irradiation technique described here permitted vanadium to be determined from the combined vanadium and chromium contributions at 1·44 MeV.

The absence of cobalt from the samples greatly simplifies analytical determination since suitable equations can be derived for irradiations carried out in two positions, one in which fast-neutron and the other in which thermal-neutron reactions predominate in the sample. The energy distribution of neutrons in the irradiation position will depend on the design of the neutron generator and its surroundings, but Fig. 1 shows the relative neutron flux at different distances from the neutron-emitting target of the sealed-tube generator used for this work. Data were obtained by securing monitors to special carriers which controlled the distance of nearest approach of the sample to the neutron source; the ordinate gives the counts under the 1·44-MeV γ-peak of ^{52}V obtained from different target elements normalized to the same neutron dose. Figure 1 shows that the fast flux, as monitored by the reaction $^{52}Cr(n, p)^{52}V$, decreases rapidly with distance from the face of the neutron emitting target, but the capture reaction $^{51}V(n, \gamma)^{52}V$ is less sensitive to position. Consequently the relative yield of the capture to the (n, p) reaction increases with distance, and conditions for the solution of the equations

$$C_T{}^A = S_{Cr}{}^A\ W_{Cr} + S_V{}^A\ W_V \tag{8}$$

$$C_T{}^B = S_{Cr}{}^B\ W_{Cr} + S_V{}^B\ W_V \tag{8A}$$

are satisfied if the sample is up against the neutron-emitting target in position A and in a higher relative thermal flux in position B; C_T is the total counts measured over

TABLE II.—DETERMINATION OF VANADIUM AND CHROMIUM OR MANGANESE AND IRON IN NICKEL-BASE MIXTURES

Sample	Vanadium		Chromium	
	Expected, %	Found, %	Expected, %	Found, %
1	5·0	4·9	15·0	15·1
2	5·0	4·6	10·0	10·1
3	5·0	5·1	5·0	5·0
4	2·5	2·7	2·5	2·4
5	1·0	1·0	1·0	1·0

Cycle (1) $T_{\mathrm{I}} = 1$ min, $T_{\mathrm{D}} = \frac{1}{2}$ min, $T_{\mathrm{C}} = 4$ min
Cycle (2) $T_{\mathrm{I}} = 2$ min, $T_{\mathrm{D}} = \frac{1}{2}$ min, $T_{\mathrm{C}} = 4$ min

Sample	Manganese		Iron	
	Expected, %	Found, %	Expected, %	Found, %
1	5·0	4·8	10·0	10·0
2	5·0	4·7	15·0	15·7
3	2·5	2·9	2·5	2·4
4	7·5	7·5	15·0	14·7

Cycle (1) $T_{\mathrm{I}} = 1$ min, $T_{\mathrm{D}} = 30$ min, $T_{\mathrm{C}} = 10$ min
Cycle (2) $T_{\mathrm{I}} = 2$ min, $T_{\mathrm{D}} = 30$ min, $T_{\mathrm{C}} = 10$ min

the 1·44-MeV peak of vanadium-52. In this work 4·3 cm of hydrogenous moderator were placed between sample and neutron-emitting target to obtain irradiation position B. This was achieved by the simple expedient of rotating the sample carrier through 180°.

A similar pair of equations to (8) and (8A) can clearly be obtained for manganese and iron, based on the measurement of the intensity of γ-rays from manganese-56.

In order to test the reliability of a double irradiation procedure for solving equations of the form (8) and (8A), samples containing either manganese and iron, or chromium and vanadium, in a nickel base were irradiated. The specific activity constants required for solution of the equations were found from the irradiation of standards consisting of single elements in a nickel matrix. Results obtained are given in Table II and can be seen to agree with expected values; also included in Table II are irradiation

TABLE III.—DETERMINATION OF VANADIUM, CHROMIUM, MANGANESE AND IRON IN NICKEL-BASE SAMPLES

Sample	Vanadium		Chromium		Manganese		Iron	
	Expected, %	Found, %	Expected, %	Found, %	Expected, %	Found, %	Expected, %	Found, %
S	4·9	5·6	20·8	19·3	4·2	4·7	3·5	3·5
T	4·1	4·3	2·6	2·5	2·3	2·9	2·2	2·4
U	3·5	3·1	4·9	4·9	1·6	1·6	5·4	5·4
V	2·0	2·3	9·5	9·2	3·0	4·1	1·8	1·6
W	4·7	4·2	1·4	1·4	1·2	1·2	3·2	3·4
X	3·7	3·6	7·5	7·6	2·6	2·8	2·4	2·7
Y	1·2	1·5	14·2	13·6	2·0	1·4	5·8	6·1
Z	1·3	1·5	17·6	16·6	3·6	4·0	3·9	3·7

Cycle (1) $T_{\mathrm{I}} = 1$ min, $T_{\mathrm{D}} = \frac{1}{2}$ min, $T_{\mathrm{C}} = 4$ min
$T_{\mathrm{D}} = 30$ min, $T_{\mathrm{C}} = 10$ min
Cycle (2) $T_{\mathrm{I}} = 2$ min, $T_{\mathrm{D}} = \frac{1}{2}$ min, $T_{\mathrm{C}} = 4$ min
$T_{\mathrm{D}} = 30$ min, $T_{\mathrm{C}} = 10$ min

(T_I), cooling (decay) (T_D) and counting (T_C) times for each irradiation cycle. The first of the two irradiations carried out on each sample took place in the lower flux position to minimize the residual activity in the sample. The 3·76-min activity of vanadium-52 was always allowed to decay before the sample was irradiated for a second time but a correction for the longer-lived manganese-56 was often required when totalling the counts in the 0·85-MeV γ-peak after the second irradiation and was calculated from a knowledge of the first count and the time between first and second counting periods.

In order to determine the four adjacent elements vanadium, chromium, manganese and iron in the same samples, the procedures for the two pairs of interfering elements were combined. Samples were counted twice in each activation cycle, once after a cooling time of $T_D = \frac{1}{2}$ min to obtain the ^{52}V count and again, when the short lived activity had decayed away, at $T_D = 30$ min to measure the ^{56}Mn activity which was usually of lower intensity.

The manganese and iron concentrations in the sample were calculated first and the manganese figure used to apply a correction to the 1·44-MeV γ-yield for ^{52}V formed from manganese by the reaction ^{55}Mn(n, α)^{52}V. Results obtained are shown in Table III, each figure being the mean of determinations carried out on at least 4 samples of each material and can be seen to show reasonable agreement with the values expected.

Zusammenfassung—Vier Elemente, Vanadium, Chrom, Mangan und Eisen wurden in Proben mit Nickel als Hauptbestandteil nach Messung der Intensität zweier γ-Linien bestimmt: der 0,85 MeV-γ-Strahlung von ^{56}Mn (aus Mn und Fe) sowie der 1,44 MeV-γ-Strahlung von ^{52}V (aus V und Cr). Die zu jedem γ-Peak beitragenden zwei Elemente wurden einzeln bestimmt an Hand von Daten, die durch zweimaliges Bestrahlen jeder Probe mit Neutronen verschiedener Energieverteilungen erhalten wurden.

Résumé—On a dosé quatre éléments, le vanadium, le chrome, le manganèse et le fer dans des échantillons à base de nickel après mesure de l'intensité de deux raies γ: la raie γ 0,85 MeV émise par le ^{56}Mn (produit par Mn et Fe) et la raie γ 1,44 MeV du ^{52}V (provenant de V et Cr). Les deux éléments contribuant à chaque pic γ ont été déterminés séparément à partir de données obtenues en irradiant chaque échantillon deux fois avec des neutrons de répartitions d'énergie différentes.

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Ge(Li) GAMMA-RAY SPECTROMETRY AS A PILOT FOR NaI(Tl) GAMMA-RAY SPECTROMETRY

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Summary—Lithium-drifted germanium semiconductor detectors give much better resolution than do thallium-activated sodium iodide detectors, but much lower sensitivity. They can often advantageously be used in conjunction with NaI(Tl) detectors, to show whether corrections must be applied for activities other than the one to be measured and to provide the necessary information for calculation of the corrections.

IN THE early days of activation analysis, post-irradiation radiochemical separations were a necessity, since no means of doing gamma-ray spectrometry were available. Separated activities were usually beta-counted with a Geiger–Müller or gas proportional counter. Such radiochemical separations, greatly developed and applied by A. A. Smales and his colleagues at Harwell, are still quite necessary in many instances (*e.g.*, Ref. 1). With the advent of the NaI(Tl) scintillation detector and the single-channel pulse-height analyser, it was found that certain elemental analyses could be performed by means of purely instrumental activation analysis, based on gamma-ray spectrometry. The subsequent availability of multichannel pulse-height analysers greatly advanced the speed and scope of the instrumental form of the activation analysis method. Step by step, these multichannel analysers were improved, from the early 20-channel vacuum-tube discriminator type to the transistorized versions, with 100–512 analysis and storage channels.

By this time, the resolution of the pulse-height analyser was so good that the limiting factor was the rather poor resolution of the NaI(Tl) detector itself. This limited the practical application of the instrumental activation analysis technique, since neutron activation of many kinds of samples of interest—but of complex elemental composition—resulted in pulse-height spectra consisting of large numbers of photopeaks, of various sizes and of various gamma-ray energies, many of which overlapped with one another. This problem has been attacked rather effectively by the development of computer programs, for resolving such complex spectra into their various radionuclide components, such as those pioneered by the Harwell group, especially by Salmon.[2]

The most recent advance in the field of gamma-ray spectrometry is, of course, the development of the lithium-drifted germanium semiconductor detector, Ge(Li). Depending on the size, shape, sensitive depth, type, and the gamma-ray energy, these detectors typically exhibit a resolution (FWHM) 10–20 times better than that of even a very good standard 75 × 75 mm NaI(Tl) detector. Once the resolution of the detector became better than that of the available pulse-height analysers, analysers with a much larger number of analysis and storage channels were soon developed: first with 1024 channels, then 2048, and now 4096 or 8192. The combination of a

15 cm^3 (10 mm depth) Ge(Li) detector and a 4096-channel analyser, such as is used in the authors' laboratory, completely resolves almost every photopeak found in the pulse-height spectra of even very complicated matrices that have been activated with neutrons in the reactor.

Unfortunately, although the presently-available, rather small Ge(Li) detectors are vastly superior to NaI(Tl) detectors in energy resolution, they are also far less efficient in their detection of gamma-rays—at least at energies greater than a few hundred keV. It is the purpose of this paper to emphasize how a high-resolution, but low-efficiency, Ge(Li) spectrometer can be frequently used very advantageously as a "pilot" for the low-resolution, high-efficiency NaI(Tl) spectrometer. A 75 × 75 mm NaI(Tl) detector is compared with a 15 cm^3 Ge(Li) one unless otherwise stated.

EXAMPLES

The idea of using a Ge(Li) spectrometer as a pilot for an NaI(Tl) spectrometer can be described best by first considering a general case, and then by giving some actual experimental examples. The general case: a sample is activated and then counted on an NaI(Tl) spectrometer, possibly producing a complicated pulse-height spectrum (many peaks) or perhaps a rather simple one. One peak appears to be due to the induced activity of interest. If the irradiation, decay, and counting times have been optimized for detection of an induced activity of that particular half-life, the probability that that peak is due to that particular radionuclide is increased. Its identity can be checked further by counting at several decay times—to ascertain whether the peak is decaying according to the expected half-life—and possibly by looking also for other gamma rays (if any) emitted by that particular radionuclide. Unfortunately, the additional counting and calculating required to check the half-life is rather time-consuming.

If it is decided that the observed photopeak is due entirely to the radionuclide of interest, the amount of the element present can be calculated by comparison with the corresponding photopeak of a standard sample of that element, activated and counted in an identical fashion. Considering (1) the large number of radionuclide species that can be formed to a significant degree, from the various chemical elements, by thermal-neutron and fast-neutron reactions, (2) the very large number of different X-ray and gamma-ray energies possibly being emitted by an activated sample, and (3) the rather poor energy resolution of the NaI(Tl) detector, it is apparent that errors can be made.

A rather extreme, but instructive, example is shown in Fig. 1. This shows the spectrum of a small sample of the rare-earth mineral, xenotime, that had been activated with neutrons in the reactor, resolved by the NaI(Tl) detector and a 0·9-cm^3 (3 mm deep) Ge(Li) detector. Starting at the low-energy end of the NaI(Tl) spectrum, it is seen that there appear to be five broad major photopeaks—of decreasing size with increasing gamma-ray energy. However, the Ge(Li) spectrum reveals that only one of these NaI(Tl) photopeaks is really a single-energy peak—the one at the highest energy. Each of the other four NaI(Tl) peaks is seen to contain contributions from gamma rays of 2, 3, or 4 different energies—in each group too close to one another in energy to be resolved by the NaI(Tl) detector.

If the only interest lay in analysing the sample for an element of which the induced activity emitted gamma rays of one of the energies falling in one of the broad multi-component NaI(Tl) peaks, an erroneous answer would, of course, be obtained if the

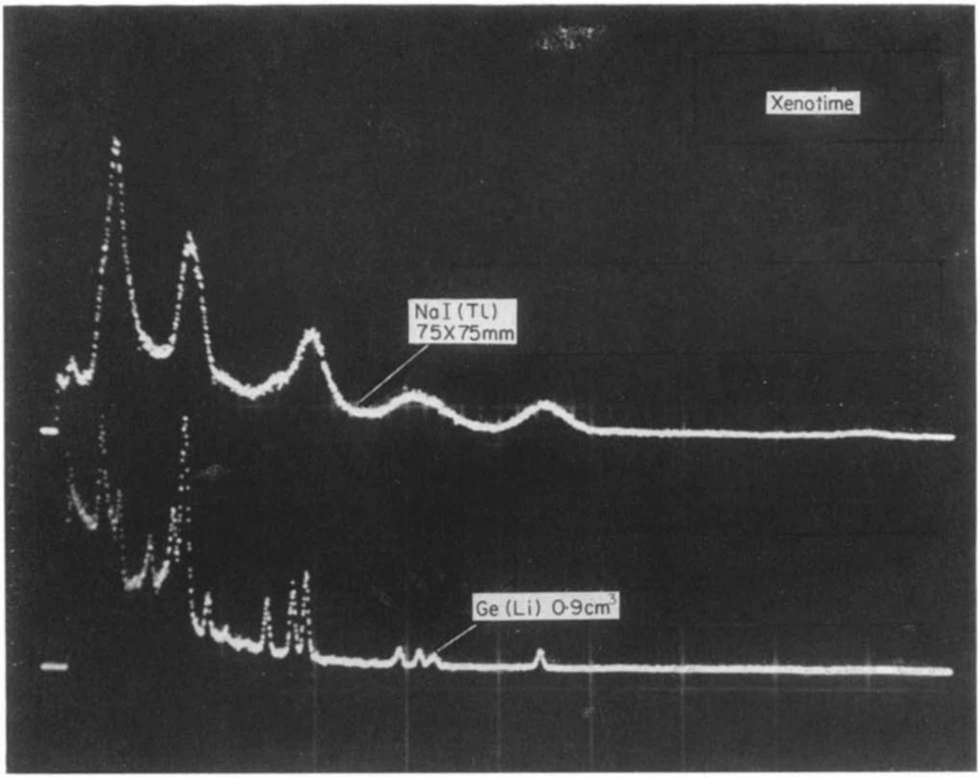

FIG. 1.—Ge(Li) pulse-height spectrum of a neutron-activated sample of xenotime.

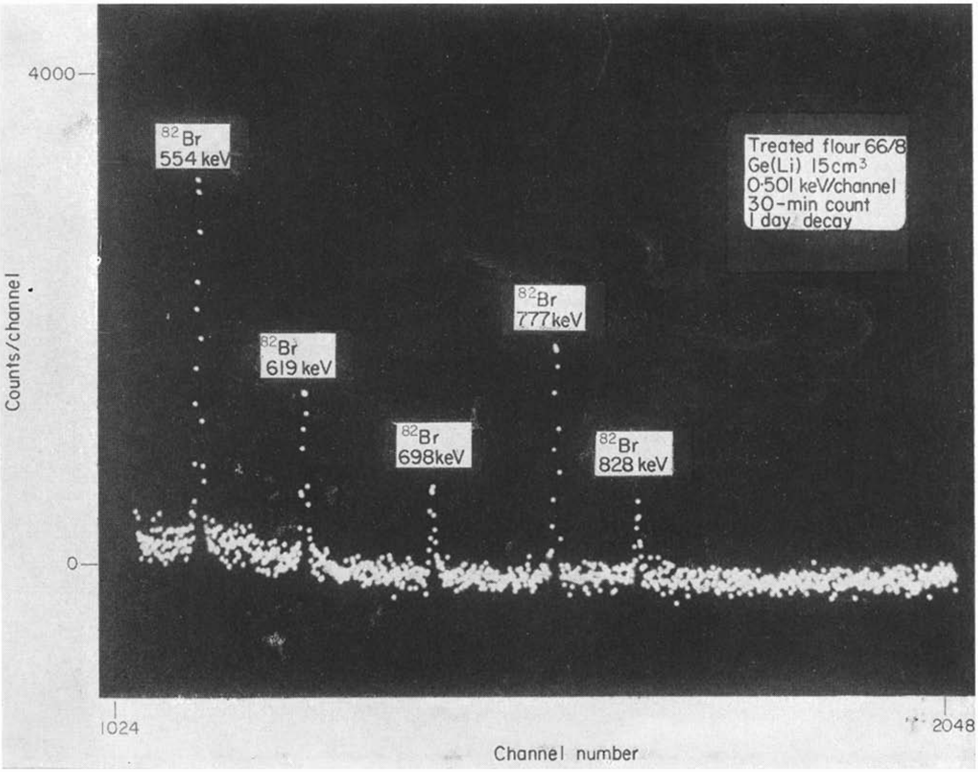

FIG. 2.—Ge(Li) pulse-height spectrum of a neutron-activated sample of flour containing 8 ppm Br.

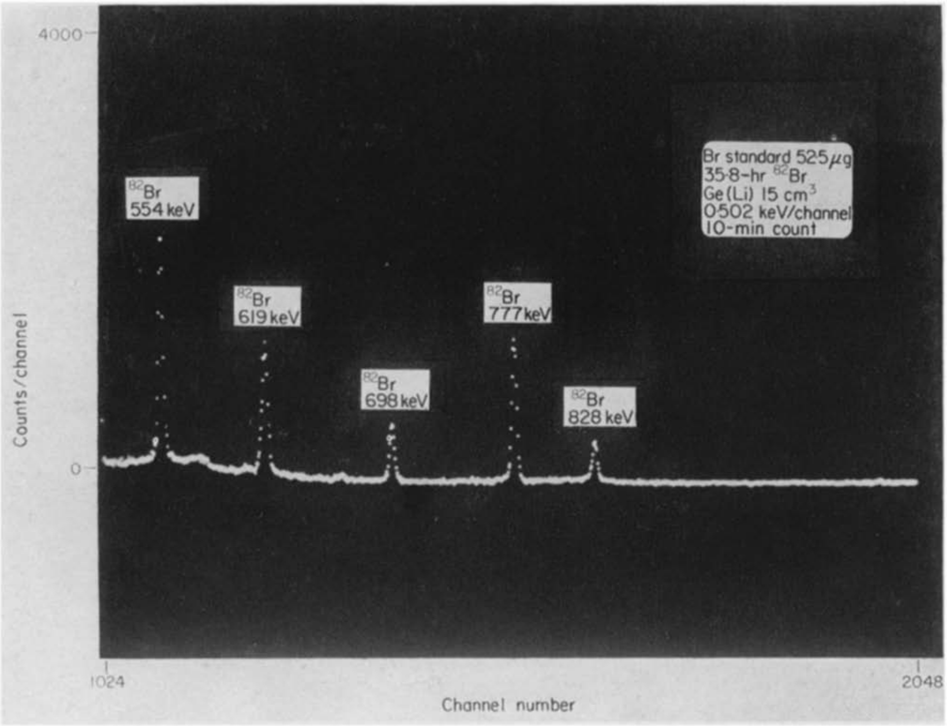

FIG. 3.—Ge(Li) pulse-height spectrum of a neutron-activated aqueous Br standard.

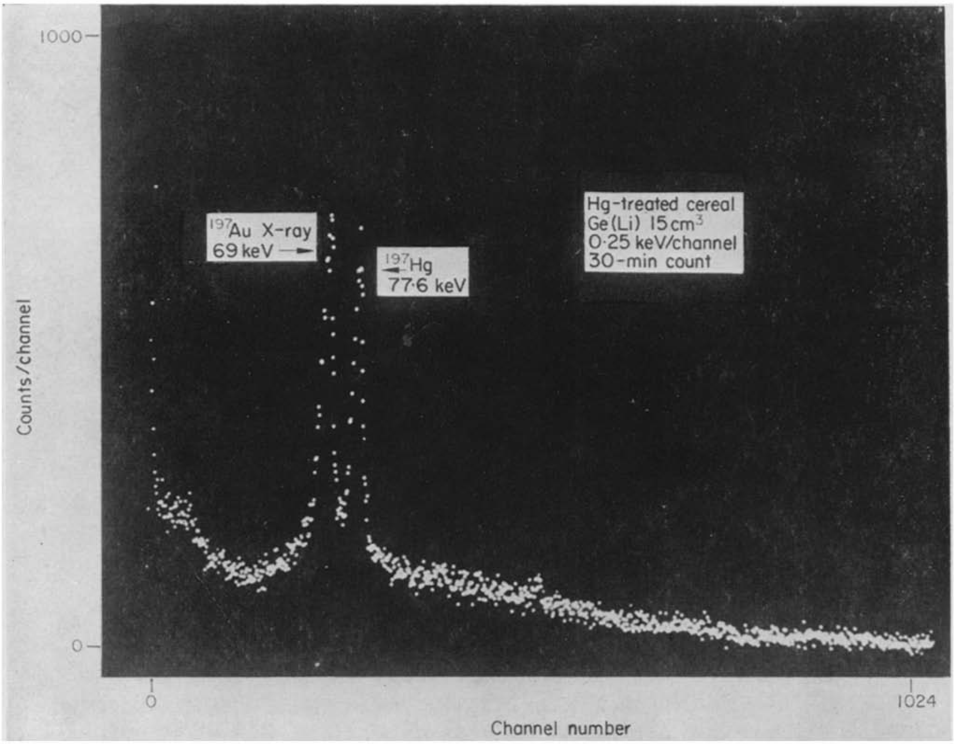

FIG. 4.—Ge(Li) pulse-height spectrum of a neutron-activated sample of flour containing 5 ppm Hg.

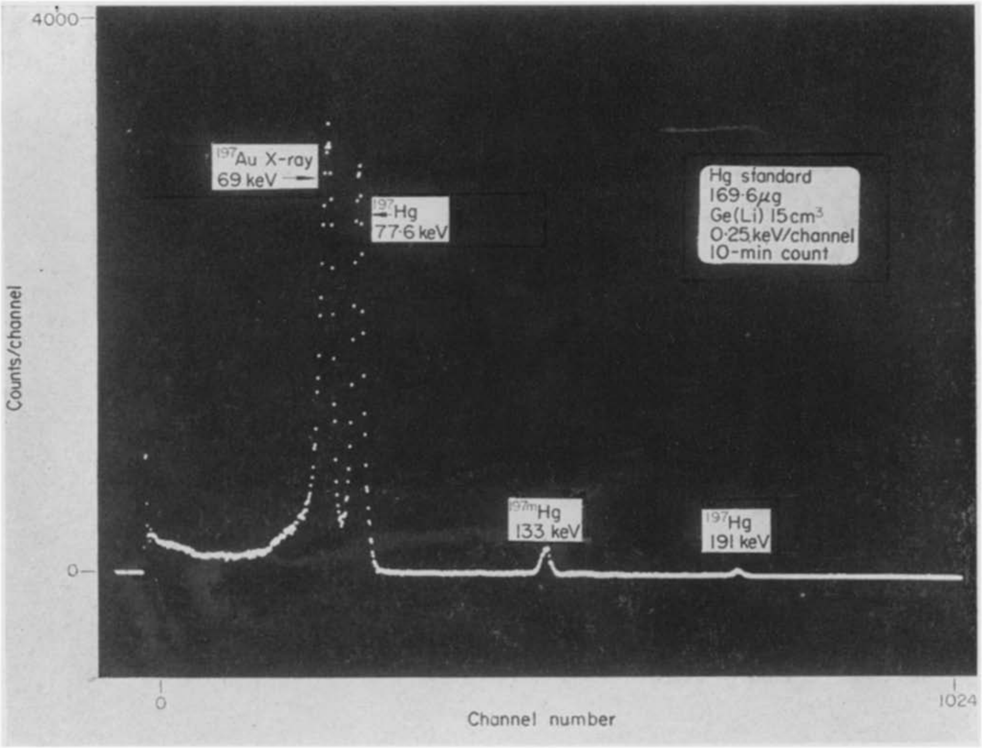

FIG. 5.—Ge(Li) pulse-height spectrum of a neutron-activated aqueous Hg(II) standard.

NaI(Tl) peak were considered to be due only to that particular radionuclide. In such a situation, (1) the use of the NaI(Tl) detector could be abandoned, and the calculations based on the Ge(Li) spectrum, (2) radiochemical separations could be used to isolate the activity of interest, (3) the data could be treated by a computer program that includes all possible contributory radionuclides, or (4) the Ge(Li) spectrum could be used as a pilot to indicate exactly which specific gamma-ray energies must be included in a weighted least-squares fitting of the entire NaI(Tl) spectrum or of that region of the one broad NaI(Tl) peak that includes the gamma ray of interest (in this example, it is assumed that the half-lives of the various interfering species are sufficiently close to that of the radionuclide of interest for simple decay not to help appreciably in solving the problem). The difficulty with resorting entirely to the Ge(Li) detector is that the counting efficiencies of such small detectors are very low at the higher gamma-ray energies, thus often requiring counting periods of an hour or more to obtain as good photopeak counting statistics as could be obtained in minutes with the NaI(Tl) detector.

An example of more specific practical interest is the instrumental determination of bromine pesticide residues in foodstuffs, by means of activation analysis using thermal neutrons. Experience at this laboratory has shown that, with a 30-min activation of a 0·5-g sample, at a thermal-neutron flux of 2×10^{12} ncm^{-2} sec^{-1}, followed by a 2–3 day cooling period before counting on a 75 × 75 mm NaI(Tl) gamma-ray spectrometer, bromine can be detected instrumentally in most foodstuffs *via* the gamma rays of 35·3-hr bromine-82. In untreated samples, the observed bromine levels are usually in the 0·1–10 ppm range.[3] In crop materials grown in soil treated with a nematocide, *e.g.*, dibromochloropropane,[4] and in grains and flour fumigated in storage with methyl bromide,[5] the bromine levels are frequently in the 10–50 ppm range, and sometimes higher. The gamma-ray spectrum of bromine-82 is complex, since this radionuclide emits gamma rays of eight different energies, in the range from 0·5 to 1·5 MeV: 0·554 (66%), 0·619 (41%), 0·698 (27%), 0·777(83%), 0·828 (25%), 1·044 (29%), 1·317 (26%), 1·475 (17%).[6] Because of their greater abundances and better detection efficiencies, the 0·554 and/or the 0·777 MeV gamma rays are usually used in the calculations. However, as can be seen in Heath's catalogue,[7] the 0·554 and 0·619 MeV peaks largely overlap, and the 0·698, 0·777, and 0·828 MeV peaks overlap. Furthermore, the two broad composite peaks (with maxima at 0·554 and 0·777 MeV respectively) are not completely resolved from one another. These five peaks essentially occupy the 0·5–0·9 MeV region of the spectrum. Therefore, there is always the possibility that the region also includes significant contributions from gamma rays from other radionuclides.

As shown in Figs. 2 and 3, this possibility can be readily checked by counting on a Ge(Li) spectrometer. In this example, a fumigated flour sample, found to contain about 8 ppm bromine, was counted on the NaI(Tl) and Ge(Li) detectors. As seen in Fig. 2, the five bromine-82 peaks (0·554–0·828 MeV) show up, completely resolved from one another, and no extraneous gamma-ray peaks are observed in the 0·5–0·9 MeV energy range. Furthermore, comparison with the Ge(Li) spectrum of an activated aqueous bromine standard (Fig. 3), reveals that the five peaks have the same ratios to one another in both the flour sample and the standard. The bromine-82 purity of this region of the spectrum having been ascertained, the broad 0·777-MeV peak in the NaI(Tl) spectra was used to calculate the bromine content of the sample.

The mean value obtained on three aliquots, in 30-min counts after 1–3 days decay, was 8·05 ± 0·93 ppm bromine (mean of 6 measurements ranging from 7·09 to 9·15 ppm). The spread of values was only partially due to counting statistics, since each count had a standard deviation equivalent to only about ±0·15 ppm bromine. In order to obtain this good a counting precision with the Ge(Li) detector it is necessary to count for 3 times as long if the counts under the three peaks at 0·698, 0·777 and 0·828 MeV are combined and for almost 5 times as long if only the 0·777 MeV peak is employed. The mean value obtained from 14 measurements using separately the 0·554 and 0·777 MeV peaks was 8·02 ± 0·54 ppm, in good agreement with the NaI(Tl) determination.

A third example is furnished by a recent analysis of a sample of flour containing about 5 ppm mercury (from seed grain, treated with a mercurial fungicide). The mercury (n, γ) product measured was 65-hr mercury-197. This radionuclide decays by electron capture, emitting predominantly 77·6 keV gamma rays and gold K X-rays (mostly at 68·8 keV).[6] With an NaI(Tl) detector, the 68·8 and 77·6 keV photons produce a single slightly broadened photopeak.[7] As can be seen in Figs. 4 and 5 these two peaks can be resolved from one another with a Ge(Li) detector. Since the spectral region included in the broad NaI(Tl) peak (*ca.* 63–82 keV) might also include some contributions from gamma rays of other radionuclides possibly present in the activated flour sample, back-scattered radiation from slightly higher-energy gamma rays (84–121 keV), and K X-rays from the elements from osmium ($Z = 76$) to bismuth ($Z = 83$) it was important to check this region with the Ge(Li) detector. It is evident from Figs. 4 and 5 that other elements in the flour do not give rise to interference and that it is safe to compute the mercury content of the sample by means of a simple photopeak area calculation, using the NaI(Tl) spectrum.

Three aliquots of the flour sample, and an aqueous mercury(II) standard, were activated for 30 min in the reactor, at a thermal-neutron flux of $1{\cdot}8 \times 10^{12}$ n. cm^{-2}. sec^{-1}. Then each was counted for 30 min, twice, on a 75 × 75 mm solid NaI(Tl) detector after a 1-day decay. From the single broad peak attributed to mercury-197, the mercury content was calculated to be 5·13 ± 0·21 ppm (with a single-count standard deviation, due only to counting statistics, of about ±0·06 ppm). The samples were also counted once for 30 min under similar conditions on the Ge(Li) detector. The mean value from these measurements was 5·13 ± 0·15 ppm. The precision is actually slightly better, probably fortuitously, than that obtained with the NaI(Tl) detector. The single-count standard deviation, based only on the counting statistics, was equivalent to ±0·16 ppm. In the Ge(Li) calculations, only the 77·6-keV peak was employed as the basis. If both the 77·6 and 68·8 keV peaks had been added together in the calculations, the single-count standard deviation, from counting statistics only, would have been lowered to about ±0·11 ppm. At such low energies, the Ge(Li) is just as efficient as NaI(Tl), but its small area decreases the geometric factor.

CONCLUSIONS

The Ge(Li) detector can be used effectively, not only as the primary counter in instrumental activation analysis gamma-ray spectrometry but also as a pilot detector, to assist in the processing of NaI(Tl) activation analysis pulse-height data. If the Ge(Li) pilot spectrum shows that the observed broad NaI(Tl) peak of interest is due entirely to the radionuclide of interest, the NaI(Tl) photopeak data can be used in a simple calculation. Advantage can thus be taken of the generally better NaI(Tl) counting statistics (or of comparable statistics from shorter counting periods). If the Ge(Li) pilot spectrum shows that the broad NaI(Tl) peak of interest also contains contributions from gamma rays of other radionuclides, these particular interfering gamma rays—and no others—can be included in a least-squares fitting calculation, to resolve the NaI(Tl) peak into its components. By reduction of the number of gamma-ray energies to be considered in the least-squares fitting calculation, greater precision and accuracy are attainable. Although the discussion has centred about the determination of one particular element of interest in a complex sample, the same approach applies also to multi-element determinations.

Zusammenfassung—Mit Lithium diffundierte Germanium-Halbleiterdetektoren geben viel bessere Auflösung als Thallium-aktivierte Natriumjodiddetektoren, sind aber viel unempfindlicher. In Verbindung mit NaJ(Tl)-Detektoren können sie oft vorteilhaft verwendet werden, um zu zeigen, ob für andere als die zu messenden Aktivitäten korrigiert werden muß, und um die zur Berechnung der Korrekturen notwendigen Daten zu erhalten.

Résumé—Les détecteurs à semi-conducteur au germanium-lithium "drift" donnent une bien meilleure résolution que les détecteurs à iodure de sodium activé au thallium, mais une beaucoup plus faible sensibilité. Ils peuvent être souvent avantageusement utilisés en liaison avec les détecteurs NaI(Tl), pour montrer si des corrections doivent être appliquées à des activités autres que celle à mesurer et apporter l'information nécessaire pour le calcul des corrections.

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ACTIVATION ANALYSIS WITH STANDARDS CONTAINING TWO OR MORE ACTIVE NUCLIDES

A COMPUTERIZED METHOD OF CALCULATION INVOLVING DECAY AND GAMMA SPECTRAL RESOLUTION

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Summary—The resolution of the gamma spectra of activities induced in materials by fast neutron, charged particle and gamma photon activation is complicated by the fact that many elements produce more than one active nuclide in significant amounts. Direct resolution by least-squares fitting of the spectra of standards is only possible in these circumstances if the standard and sample spectra are obtained at the same time after irradiation, as the shapes of the standard spectra change with time. An alternative to the practical collection of spectra in this way is the correction of the standard spectra to the mid-time of counting of a sample spectrum. This may be achieved by recording spectra for a standard at different times and resolving the decay curves obtained for each channel on the basis of the half-lives of the component nuclides, which may be decay-independent or related or both. From the component nuclide count-rates in each channel at some arbitrary time, the standard spectrum at the time of counting of the sample can be generated and then used in a conventional least squares-fit of the sample spectrum. A FORTRAN IV program has been written to carry out this type of calculation on an IBM 360/65 computer. The feasibility of using this method is demonstrated by its application to activation analyses involving standards containing decay-related and independent nuclides.

THE application of fast neutrons, charged particles and gamma photons as irradiating species in activation analysis has increased greatly in recent years.[1,2] These energetic species often induce significant amounts of two or more active nuclides in an irradiated element. In an activation analysis the presence of such elements leads to difficulty in the interpretation of the counting data.

The most widely applied counting method in activation analysis is gamma spectrometry; this frequently involves the use of a sodium iodide detector and a pulse-height analyser, though other detectors, particularly lithium-drifted germanium diodes, are also used. A typical non-destructive thermal neutron activation analysis comprises simultaneous irradiation of the sample and standards followed by successive collection of their gamma spectra. The composition of the sample may then be obtained by computer resolution of its gamma spectrum in terms of proportions of the standard spectra; the mathematical technique most widely adopted for this purpose is the least-squares method.[3–7] The application of this method of spectrum resolution is conditional on the shape of the standard spectrum remaining constant with time. Standards containing only one active nuclide have spectra that fulfil this condition, whereas those containing two or more do not. Consequently the adoption of successive counting of sample and standards precludes this method of spectral resolution if standards containing two or more active nuclides are involved, unless these nuclides have long or virtually identical half-lives.

The difficulty caused by standards having two or more active nuclides may be partially avoided by discarding part of the spectral information before carrying out a least-squares fit. One approach is to restrict the spectral region fitted, to one of sufficiently high energy for photopeak contributions from all but one nuclide in a standard to be excluded. Another approach is to delay counting until all nuclides but one in a standard have decayed to insignificant levels. Though both of these techniques are commonly applied they suffer the disadvantage of being liable to eliminate counting information on some elements and so prevent their determination.

If the samples and standards are counted at the same time after irradiation the difficulties associated with spectrum resolution involving standards containing two or more active nuclides are eliminated. A method of achieving this is by irradiating and counting the samples and standards individually on a strictly repeated time schedule. Anders and Beamer[8] used this technique to accumulate spectra but adopted a stripping method for sample spectrum analysis. This experimental procedure has been used in combination with least-squares spectrum analysis by Korthoven, Wechter and Voigt in the photon-activation analysis of gadolinium and europium bronzes.[9] An interesting development of this basic method was introduced by Hull and Gilmore for the fast neutron activation analysis of lubricating oils.[10] They obtain a series of spectra for each sample and standard at fixed times after irradiation and then identify the photopeak region to be used in the subsequent mathematical analysis. The series of counts in each of these spectral regions for each standard is a complex decay curve formed by the independent decay of the component nuclides present and is resolved into the individual count-rates at some arbitrary zero by a least-squares fit based on the half-lives of the component nuclides. From their count-rates a decay-smoothed total count-rate is regenerated for each region of each standard at each time. These values are then used in the analysis of a series of decay-related sample spectra, broken down into identical spectral regions, either by an iterative stripping procedure or by an overall least-squares fit.

As the last method is restricted to counts collected on a fixed time schedule the decay part of the analysis merely acts as a smoothing technique for the standard data and while this improves the overall result it is not essential to the sample spectrum analysis. If however the samples and standards had been irradiated simultaneously and each counted several times successively, this type of decay resolution could be used to obtain the standard spectra at the time of counting of a sample and consequently allow a normal least-squares analysis of the sample spectrum. Rather than restrict the decay resolution to channel groups we have applied the method to each channel in the series of spectra accumulated during the decay of each standard, and so are able to regenerate each standard spectrum at any desired time, on the basis of the calculated component nuclide count-rates in each channel at some arbitrary zero time. A further development is the extension of the decay analysis method to standards containing related as well as independently decaying nuclides.

A computer program, DECSPEC, has been written to carry out these calculations on an IBM 360/65 computer. The feasibility of using this method is demonstrated by its application to activation analyses involving standards containing decay-related and independent nuclides.

MATHEMATICAL ANALYSIS OF COUNTING DATA

The mathematical analysis of the counting data accumulated during an activation analysis of the type under consideration falls into two parts. The first is the analysis of the series of spectra obtained during the decay of each standard in order to obtain the standard spectra as they would be at the time the sample is counted. The second is the analysis of the sample spectrum in terms of proportions of the corrected standard spectra.

Correction of the standard spectra

The series of n spectra, each of m channels, accumulated for a standard during its decay can be broken down into a group of m decay curves each with n observations. Providing these decay curves have been formed by independently decaying nuclides, the observations in any one of them can be considered to be represented by a set of equations

$$y_n = \sum^{k} x_k \exp(-\lambda_k t_n) \tag{1}$$

where y_n is the observed counting rate at time t_n, the λ_k decay constant of the kth radioactive nuclide present, and x_k its counting rate at time $t = 0$. The condition $n \geqslant k \geqslant 1$ must apply, where k is the number of nuclides fitted. The application of the least-squares principle requires that the variance of each observation should be the same. Since this is not so, each observed counting rate, y_n, must be weighted by a factor w_n, which is the inverse of the variance of the observed count, allowance having been made for the background count:

$$w_n y_n = \sum^{k} w_n x_k \exp(-\lambda_k t_n) \tag{2}$$

These equations can be written in matrix form as

$$W . y = W . A . x \tag{3}$$

where y and x are vectors, W is a diagonal weighting matrix and A is a matrix having A_{nk} elements where $A_{nk} = \exp(-\lambda_k t_n)$. By minimizing the sum of the squares of the errors in y it can be shown from the theory of multilinear regression[11] that the resulting normal equations, leading to the best estimates for x, are

$$A^T . W . y = A^T . W . A . x \tag{4}$$

where A^T is the transpose of A. Solution of the equations, rearranged in the form

$$x = [A^T . W . A]^{-1} . A^T . W . y \tag{5}$$

gives the count-rates of the individual component nuclides at $t = 0$. The inversion of the matrix $[A^T . W . A]$ is carried out by the Choleski method[12] using "double precision arithmetic". An advantage of the matrix method of solution is that the variances of the vector x occur on the diagonal of the inverse matrix $[A^T . W . A]^{-1}$, and consequently are readily available.

When the calculation of the component count-rates in each channel at time $t = 0$ has been completed, these count-rates can be decayed to those applicable at the counting time of a sample. Reassembly of the standard spectrum at the time of counting of the sample now merely involves the addition of the decay-corrected component count-rates within each channel. This standard spectrum is ready for subsequent use in the resolution of the sample spectrum.

This method of channel decay resolution is not directly applicable to standards that contain related decaying species. In order to apply the method to a two-component system in which one component is the daughter of the other, the observed counting rate y_n at time t_n, can be considered to be

$$y_n = x_a \exp(-\lambda_a t_n) + x_b \exp(-\lambda_b t_n) + x_{ab} \frac{\exp(-\lambda_a t_n) - \exp(-\lambda_b t_n)}{\lambda_b - \lambda_a}. \tag{6}$$

This equation is similar to equation (1) except for the inclusion of an extra count-rate term, x_{ab}, the count rate of *b* derived from *a*, with its special decay coefficient. While it is not essential to include the term $(\lambda_b - \lambda_a)$ in the decay coefficient its presence conveniently keeps the coefficient positive for positive values of t_n. As equation (6) is of the same form as equation (1) it may be solved in a similar manner for x_a, x_b and x_{ab} at $t = 0$. Decay-correction to the time of counting of a sample is carried out as previously described, to obtain the desired standard spectrum; all decay adjustments to x_{ab} are made using its special decay coefficient

$$\frac{\exp(-\lambda_a t_n) - \exp(-\lambda_b t_n)}{\lambda_b - \lambda_a}.$$

For standards containing active nuclides with more complicated decay relationships, other expressions can be set up for the observed counting rate, y_n. These are similar to equation (6) as they also include extra terms which account for activities derived by decay of other nuclides. However, it must be noted that the number of terms required rises rapidly with the number of successive decays involved, making the decay resolution increasingly difficult. Because of this we are not at present attempting to extend the application of this method to such cases.

Sample spectrum analysis

When all of the standard spectra have been corrected to the time at which a sample is counted, the analysis of that sample spectrum in terms of proportions of the standard spectra may proceed. If the sample contains *j* standards each of *m* channels, the count rate of the *i*th channel is

$$c_i = \sum^{j} l_{ij} b_j \tag{7}$$

where l_{ij} is the experimentally determined fraction of the *j*th standard expected in the *i*th channel, and b_j is the amount of the *j*th standard. An equation of this type exists for each of the *m* channels, and these equations may be written in the following matrix form,

$$P\,.\,r = s \tag{8}$$

where *r* and *s* are vectors with b_j and c_m elements respectively, and *P* is a rectangular matrix having P_{mj} elements, where $P_{mj} = l_{mj}$. The application of the least-squares principle, as in the decay analysis, requires the weighting of the observations. For this purpose a channel weighting factor, v_i, is applied, which is the inverse of the count in that channel, allowance having been made for the background count. If *V* is the diagonal weighting matrix, then the weighted matrix equations are

$$V\,.\,P\,.\,r = V\,.\,s. \tag{9}$$

Minimization of the sums of the squares of the errors in s again gives a set of normal equations which lead to the best estimates for r. These equations are

$$P^{T} . V . P . r = P^{T} . V . s \tag{10}$$

where P^{T} is the transpose of P. The solution of these equations

$$r = [P^{T} . V . P]^{-1} . P^{T} . V . s \tag{11}$$

yields the amounts of the individual standards present. The inversion of the matrix $[P^{T} . V . P]$ is again carried out by the method described in the section on the correction of the standard spectra.

In order to test the goodness of the spectral fit the observed and predicted errors are compared. For this purpose the sum of the weighted squares of the differences between the observed and fitted count-rates for each channel, χ^2, is calculated:

$$\chi^2 = \sum^{m}(c_i - c_i^*)^2 v_i \tag{12}$$

where c_i^* is the calculated count-rate of the ith channel. The "expected" value of χ^2 is the number of degrees of freedom $(m - j)$. The ratio of these quantities, R, is

$$R = \frac{\chi^2}{(m - j)} \tag{13}$$

and should be approximately equal to unity as $(m - j)$ is large; the number of degrees of freedom in our experiments was about 100 and is generally of that order of magnitude.

In practice the value of R associated with a good fit is normally somewhat larger than one. While the fit in these circumstances is acceptable, the variances of the best values for the amounts of the individual standards present should be increased by a factor R.

EXPERIMENTAL

Computation

The FORTRAN IV program, DECSPEC, for carrying out the calculations was written for use with an IBM 360/65 computer.

Initially the program reads in a background spectrum with its live time of count.

After reading in the number of standards involved, the first half of the program estimates for each of these in turn the component count-rates in each of their channels at an arbitrary zero time. To accomplish this the weight of each standard is read plus the number of component nuclides it contains, with their half-lives and whether or not any of them are decay-related. Then this is followed by the spectra obtained during the decay of the standard, each with its associated chronological time of cessation of count, and live and real times of count. The time of count for a spectrum is taken as the period from the arbitrary zero to the mid-point of its real time of count. Each spectrum is converted from counts per channel into count-rates per channel, corrected for background. When this information has been accumulated the program completes this section of the calculation, printing out and storing for every standard the component count-rates in each of their channels at zero time, plus the errors of those count-rates expressed in per cent. This information can also be presented in graphical form if desired.

The second half of the program initially reads in the number of samples to be analysed. For each sample its weight and three associated counting times are read in. Then the sample spectrum counts are read and are converted into count-rates per channel, corrected for background. The time of count of the sample is then calculated as indicated for the standards. Each standard spectrum is then corrected from zero time to the time of counting of the sample and the spectral fit is carried out. The principal answers printed out are the amounts of each standard present in a sample plus the statistical errors of these amounts, expressed in per cent. Additional items of output are χ^2 and R, the ratio of the observed to predicted errors, and these, with graphical representations of the sample fitted and difference spectra, allow a rapid human assessment of the goodness of a fit. To enable the data used to be checked, all input data are printed out.

All of the data can be presented to the computer as cards, many of which are produced automatically from the counting equipment. However, the program allows for the spectral data to be loaded on paper tape if desired. If necessary the program will correct the raw spectral data for drift errors, before the main calculations.

Irradiations

All irradiations were carried out in the Harwell reactor BEPO, using a "rabbit" irradiation facility.

Counting apparatus

The gamma spectrometer used consisted of a 75 × 75 mm sodium iodide detector and a Laben 512-channel analyser with an internal live-timer and external facilities for recording real time and chronological time. The gamma spectrometer was stabilized as described by Carter.[13] The spectral data could be punched out on 8-hole paper tape with a Westrex (BRPE 110) punch or on cards with an ICT card punch. The real time, live time and chronological time could also be punched out on cards.

Analysis of samples

The samples were simulated by mixing known amounts of irradiated standards. The geometry of samples and standards was made identical before counting at appropriate intervals during their decay.

RESULTS AND DISCUSSION

The example analyses have been chosen because they illustrate important features in the application of the method rather than because they are of great practical significance.

Analysis of copper/magnesium mixtures

Thermal neutron irradiation of copper and magnesium leads to the production of the isotopes shown in Table I. Irradiations of about 10 min are optimal for the production of magnesium-27. For such irradiations copper standards will contain comparable amounts of copper-64 and copper-66 during the immediate post-irradiation period when the magnesium-27 must be measured. If the gamma spectrum of the sample over the energy range 0·4–1·4 MeV is used in the spectral analysis copper must be treated as a two-component standard. The results of the analysis of a copper/magnesium mixture by the proposed method are shown in Table II, as are results obtained by direct least-squares fitting of copper and magnesium spectra collected 1·5 min before and after the sample spectrum; two copper results are shown for the latter method, one obtained by making a simple decay correction to the copper spectrum on the basis of a 5·1-min half-life, the other on a half-life of 12·9 hr. The results obtained by the proposed method indicate that the decay correction

TABLE I.—ISOTOPES PRODUCED BY THERMAL NEUTRON IRRADIATION OF COPPER AND MAGNESIUM

Parent isotope	Product isotope	Half-life	Energy of principal gamma rays, *MeV*
^{26}Mg	^{27}Mg	9·5 min	0·84, 1·01
^{63}Cu	^{64}Cu	12·9 hr	0·51,* 1·34 (weak)
^{65}Cu	^{66}Cu	5·1 min	1·04

* Positron annihilation

TABLE II.—COPPER/MAGNESIUM RESULTS

Method of calculation		Ratio of calculated composition: known composition, with counting errors Cu	Mg	Ratio of observed to predicted errors
Proposed method		0·998 ± 0·010	1·012 ± 0·015	1·33
Direct least-squares fit	($t_{1/2}$ = 5·1 min)	1·105 ± 0·014	0·946 ± 0·020	2·64
	($t_{1/2}$ = 12·8 hr)	0·903 ± 0·012		

method used to produce the standard spectrum is working successfully. On the other hand the results obtained by the direct fitting method show the significance of the change in spectral shape of the copper standard even when counted only 1·5 min before the sample.

Analysis of bromine/iodine mixtures

Bromine and iodine produce the active nuclides shown in Table III on irradiation with thermal neutrons. A 30-min irradiation was used for the analysis of a bromine/iodine mixture. The disintegration rates for the three isotopes present in 1 mg of bromine at the end of such an irradiation are indicated in Fig. 1. The predominant isotope present is bromine-80, while bromine-80m and bromine-82 have relatively small initial disintegration rates. After the end of the irradiation the bromine standard, for the purpose of our method of calculation, must be considered to contain four component nuclides, bromine-80, bromine-80m, and bromine-82 that decay simply with half-lives of 18 min, 4·5 hr and 36 hr, and bromine-80 which obeys a complex decay function. However, because of the low energy of the gamma emission from bromine-80m, this nuclide may be omitted from the calculation if a spectrum threshold of about 0·3 MeV is chosen. The results presented in Table IV were obtained by choosing a spectral energy range of about 0·3–1·1 MeV and omitting bromine-80m from the calculations. Normally when dealing with standards containing decay-related nuclides we adopt the practice of making zero time equal to the time of the end of the irradiation, as the count-rates of the components returned for this time are the simplest to check by inspection. In this experiment standard and sample spectra were collected at intervals over a period of about 7 hr, the frequency being highest in the early stages. The analysis of any of the sample spectra leads to a value for bromine which is in good agreement with the expected value; the answers for iodine are similarly good for those spectra containing a significant iodine-128 contribution.

TABLE III.—ISOTOPES PRODUCED BY THERMAL NEUTRON IRRADIATION OF BROMINE AND IODINE

Parent isotope	Product isotope	Half-life	Energy of principal gamma rays, *MeV*
^{79}Br	^{80m}Br	4·5 hr	0·04, 0·05
^{79}Br	^{80}Br	18 min	0·51,* 0·62
^{81}Br	^{82}Br	36 hr	0·55, 0·62, 0·78, 1·04, 1·32
^{127}I	^{128}I	25 min	0·44, 0·53

* Positron annihilation

Results were also calculated for some of the sample spectra by fitting bromine and iodine standard spectra obtained immediately before and after the first sample spectrum; decay-correction of these iodine and bromine standard spectra was based on half-lives of 25 min and 18 min respectively. As expected, the results decrease in reliability with time because of the changing shape of the bromine standard spectrum and the changing half-life of its bromine-80 component. These results are not enormously in error, as the bromine standard is dominated by the bromine-80 contribution in the immediate post-irradiation period, at which time it behaves essentially as a one-component standard; even so the goodness of fit rapidly becomes less satisfactory.

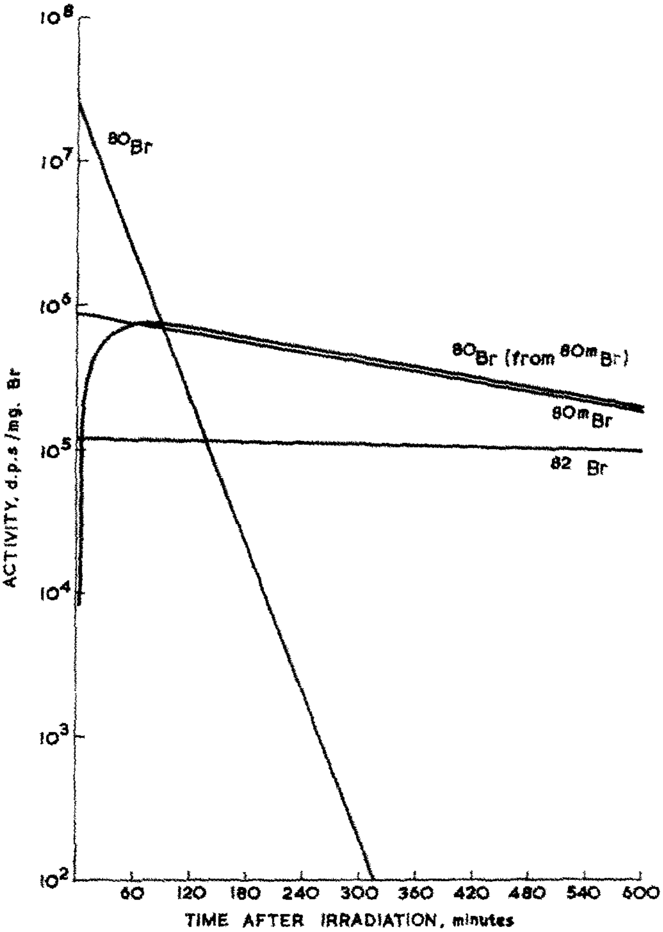

FIG. 1.—The active nuclides produced by a 30-min thermal neutron irradiation of bromine and their subsequent decay.

From Fig. 1 it can be seen that decay resolution of the bromine-80 derived from bromine-80m, and of bromine-80m itself can only be achieved by analysis of the total decay curve up to about 1 hr after cessation of irradiation, as after that time their decay functions rapidly become identical. This type of situation occurs for all decay analyses involving decay-related nuclides, because the daughter growing in

TABLE IV.—BROMINE/IODINE RESULTS

Method of calculation	Time of sample count after irradiation, *min*	Ratio of calculated composition: known composition, with counting errors		Ratio of observed to predicted errors
		Br	I	
Proposed method	13·66	1·006 ±0·006	1·016 ±0·013	1·54
	19·64	1·005 ±0·006	1·000 ±0·015	1·76
	29·10	1·007 ±0·003	0·998 ±0·008	1·48
	356·76	0·989 ±0·006	N.P.	2·33
	404·40	0·998 ±0·006	N.P.	2·68
Direct least-squares fit	13·66	1·024 ±0·007	1·027 ±0·017	2·66
	19·64	1·079 ±0·011	1·013 ±0·023	4·16
	29·10	1·186 ±0·018	1·013 ±0·035	29·8

N.P., None present

ultimately decays with its own or its parent's half-life. Consequently, for systems in which this distinction is important, adequate measurements must be made before this limiting decay relationship becomes operative.

Irrespective of whether decay-related or independent nuclides are involved in a decay analysis, the factors which tend to lead to poor resolution of a component do not prevent correct adjustment of the standard spectrum. For example, if a component is a minor contributor it is liable to be determined with a poor precision, but as its contribution is small its influence on the overall error of the standard spectrum is also small. Another example is when nuclides with similar half-lives are present; even though this may lead to large inaccuracies in the amounts of the individual nuclides the estimate of their sum will be accurate and so will the standard spectrum to which it contributes.

No correction is made, in our method of calculation, for the error incurred by assuming that the mean count-rate for a counting period occurs at its mid-time. Rather than correct the mid-time count-rates, we have kept this error small by counting for periods that are small relative to the half-lives of the nuclides present.

In its present form our method of calculation is restricted to the resolution of one spectrum at a time from a series of spectra collected for a single sample. A method for calculating isotope activities from a series of decay-related gamma spectra has been described recently by Yamamoto.[14] This type of calculation could be used in conjunction with the decay part of our method to enable a series of spectra from a single sample to be included in an overall least-squares fit. By this means an improved estimate should be obtained for those elements that have similar spectra but dissimilar half-lives.

CONCLUSIONS

The activation analysis of samples through the resolution of their gamma spectra by the least-squares fitting of proportions of the spectra of standards from which they are composed, is subject to a restriction when the standards contain more than one active nuclide. This restriction is that the sample and standard spectra must be collected at the same time after irradiation because the spectral shape of standards containing two or more active nuclides changes with time. If sample and standard spectra are collected successively and a fit is carried out, the determined sample composition is erroneous and the spectral fit poor. An alternative to the practical expedient of physically counting the sample and standards at the same time, when dealing with this type of activation problem, has been shown to be the correction of the standard spectra to their shapes at the time of counting of the sample. This correction method, based on decay resolution of a series of spectra obtained during the decay of a standard, has been demonstrated to be effective for standards containing either decay related or independent nuclides or both. The subsequent use of such corrected standard spectra in the resolution of a sample spectrum leads to an accurate assessment of the sample composition. This method of calculation should be of use in fast neutron, charged particle and gamma photon activation analysis particularly when simultaneous activation of sample and standards is employed.

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Zusammenfassung—Die Auflösung der Gammaspektren der Aktivitäten die durch Aktivierung mit schnellen Neutronen, geladenen Teilchen und Gammaquanten im Material induziert werden, wird durch die Tatsache kompliziert, daß viele Elemente mehr als ein aktives Nuklid in nennenswerter Menge liefern. Direkte Auflösung durch Anpassen der Spektren von Standards nach der Methode der kleinsten Quadrate ist unter diesen Umständen nur möglich, wenn die Spektren von Probe und Standard zur selben Zeit nach der Bestrahlung aufgenommen werden, da die Form der Standardspektren sich mit der Zeit ändert. Statt der Sammlung von Spektren auf diese Weise kann man sie Standardspektren auf die Mitte des Zeitintervalls korrigieren, in der das Probenspektrum gezählt wird. Dies kahn man erreichen, indem man die Standardspektren zu verschiedenen Zeiten mißt und die Abklingkurven in jedem Kanal auf Grund der Halbwertszeiten der darin enthaltenen Nuklide aufteilt, die in ihrem Zerfall unabhängig, voneinander abhängig oder beides sein können. Aus den zusammengesetzten Zahlraten der Nuklide in jedem Kanal zu einer willkürlichen Zeit kann man das Standardspektrum zur Zeit der Zählung der Probe erhalten und dem Probenspektrum in üblicher Weise nach der Methode der kleinsten Quadrate anpassen. Dur Durchführung dieses Rechenvor gangs auf einer Rechenmaschine IBM 360/65 wurde ein FORTRAN IV-Programm geschrieben. Daß diese Methode anwendbar ist, wird an Hand von Aktivierungsanalysen nachgewiesen, in deren Standards im Zerfall voneinander abhängige und unabhängige Nuklide vorkommen.

Résumé—La résolution des spectres gamma d'activités induites dans des produits par activation aux neutrons rapides, particules chargées et photons gamma est compliquée par le fait que de nombreux éléments produisent plus d'un nucléide actif en quantités notables. La résolution directe par ajustement aux moindres carrés des spectres des étalons n'est possible dans ces circonstances que si les spectres de l'étalon et de l'échantillon sont obtenus au même moment après irradiation, les allures des spectres de l'étalon changeant avec le temps. Une autre possibilité pour la collection pratique des spectres dans cette voie est la correction des spectres étalons au temps médian de comptage d'un spectre d'échantillon. Ceci peut être réalise en enregistrant les spectres pour un étalon à des temps différents et en résolvant les courbes de désintégration obtenues pour chaque canal sur la base des demi-vies des nucléides constituants, qui peuvent être indépendants de la désintégration ou y être rattachés ou les deux. A partir des cadences de comptage du nucléide constituant dans chaque canal à un temps arbitraire, le spectre étalon au temps de comptage de l'échantillon peut être produit et utilisé alors dans un ajustement aux moindres carrés ordinaire du spectre de l'échantillon. On a rédigé un programme FORTRAN IV pour mener ce type de calcul sur une calculatrice électronique IBM 360/65. La possibilité d'utilisation de cette méthode est démontrée par son application aux analyses par activation comprenant des étalons contenant des nucléides rattachés à la désintégration ou indépendants.

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DEVELOPMENT AND INFLUENCE OF AUTOANALYSERS AND DATA PROCESSING IN ANALYTICAL CHEMISTRY

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Summary—The present and future developments and influences of autoanalysers and data processors in analytical chemistry are critically evaluated. Rapid developments can be expected in the processing of routine chemical analyses and in the evaluation of data from physicochemical instrumentation.

THE most consistent developmental theme in chemical analysis in the period 1945–1965 was the application of increasingly sophisticated physico-chemical instrumentation to problems associated with the great range of new materials in science and technology. In particular, analytical chemists became more involved in a wide range of trace element analyses embracing the techniques of electrochemistry, spectrophotometry, spectroscopy, chromatography and radiochemistry.

The work of A. A. Smales and his group extended over all of these areas. Smales not only greatly influenced analytical chemistry in the United Kingdom by the applications of modern physico-chemical instrumentation, but he also influenced developments in other countries by a series of notable publications and lectures on such topics as neutron-activation analysis. Those who have worked with Smales's group as visiting scientists also benefited greatly and promoted many of the ideas and developments in their own countries.

The most probable developmental theme in chemical analysis for a second period of similar length, 1965–1985, is that of autoanalysers and data processing. This is not to say that such techniques will replace the present integrated complex of physico-chemical instrumentation and more classical "wet" methods, but rather that this will greatly influence the throughput of data arising from instruments and repetitive determinations. Already, small inexpensive digital computers are firmly established for the control and data-handling of mass spectrometers, gamma-ray spectrometers and other instruments. There has also been a rapid increase in the number of publications on autoanalysers during the past two years. Proceedings of recent symposia[1,2] and some reviews[3,4] illustrate the trend.

Early developments in continuous analysers

Considerable interest in continuous methods of analysis occurred some 10–15 years before the appearance of relatively inexpensive and reliable commercial autoanalysers. For example Siggia's book[5] described the commercial equipment for continuous analysis which was available in 1958. Significant contributions to this field were made by U.S.A.E.C. establishments in the mid-1950's. Hanford Atomic

Products Operation,[6] Idaho Chemical Processing Plant[7] and Oak Ridge National Laboratory[8] had extensive programmes for the development of continuous analysers and monitors in 1955–1958.

Following the introduction of the "Autoanalyser"[9] in 1957, interest in the applications of continuous solution analysers spread to biomedical and industrial chemistry. The early developments in Europe were not as extensive or as well documented. Commercial continuous volumetric analysers were available in the U.K. in the late 1950's.[10,11] Some of the earlier U.S.S.R. instruments have been described by Balashov,[12] French instruments by Curillon[13] and Regnaut,[14] and U.K. instruments by McGowan.[4] Many of the early European instruments were also used in the atomic energy industry.

The performance of earlier continuous analysis systems was closely related to the reliability of certain mechanical components. The majority of automatic valves and glands and volume-measuring systems for both gases and liquids were unreliable. Leaking or sticking valves and glands, and corrosion problems were much in evidence. Automatic volume measurement using barrel-and-piston type pipettes lacked reliability and precision. In addition, high analyser system-volumes led to lags in signals and contamination or carry-over problems. Most of these problems have now been solved with the commercial availability of reliable, corrosion-free, leakproof automatic valves and the accurate miniature micro-metering pumps based on the peristaltic principle. Peristaltic pumps can have infinitely variable flow-rate over a 100-fold range, with a precision of better than 0·5% throughout.[15] This type of pump, used for the metering of well-mixed air–solution streams, has revolutionized the development of autoanalysers.

Application of computers in chemical analysis

It is a difficult task for the analytical chemist to evaluate the extensive literature on computer applications. There is an increasing number of papers on analytical chemistry computer applications in a few well-known analytical chemistry journals. For example, the subject index of *Analytical Chemistry* lists 6 such entries in 1962, 16 in 1964 and 21 in 1966. On the other hand there are no computer applications listed under a separate heading in *Analytical Abstracts* 1966 Annual Index. However, the industrial interest in computers for process control, and hence also in the control of on-line analytical instrumentation, is well in evidence in several applied chemistry journals. The well-known annual reviews by Williams,[16] on computers and process control, provide many examples of applications to chemical analysis.

Computer applications in chemical analysis fall into two broad categories.

(1) The semi-isolated processing of data in computers sited away from the laboratory.

(2) The integration of computers with physico-chemical instrumentation or with in-line instrumentation and plant control.

In the first case, the analytical chemist is no different from any other scientist using a central computer for data processing. In the second case, chemical requirements influence the applications and there is generally a direct link between the computer and the instruments. One of the most significant developments in the use of laboratory physico-chemical instrumentation is concerned with relatively small, inexpensive data-storage and input/output devices.[17] With many instruments such as mass spectrometers, the chemist needs a fast turn-round time for processing experimental data. This cannot be easily achieved by separate punching of data and processing. The problem can be overcome by using small data stores attached to the instrument and linked to a time-shared central computer station. Alternatively, individual small computers can be included in a grouping of three or four instruments or for control of a process, including the on-line instruments.

Another recent development of interest to analytical chemists is the use of special purpose analogue computers[18] for the rapid resolution of overlapping peaks in experimental curves. Many analytical techniques such as chromatography, electrophoresis and spectroscopy produce curves which are sums of peaks or distribution functions. While other methods involving hand calculation or digital computers can be used for curve resolution, they either take more time or are not as convenient as a curve-resolver, which can be used by non-technical personnel.

Need for automation

It is comparatively easy to prove that the automation of chemical analysis and use of computers for data processing and process control is essential for large industries. However, it will be some years before such methods have an appreciable impact on the research laboratory or the smaller industrial laboratory.

Squirrell[11] and Kehoe[19] provide interesting discussions concerning when and why chemical analysis should be automated and why on-line analysis is now considered imperative. The main advantages of automated chemical analysis compared with conventional or batch chemical analysis include saving of time, improved output of results, elimination of personal bias, reduced labour costs and generally improved precision. On the other hand, some disadvantages include higher cost of basic equipment, necessity for more frequent quality checks, rapid servicing, lower accuracy and the general restriction to a particular application. Most of these disadvantages are outweighed by the advantages.

It therefore seems likely that in the laboratory, automated chemical analysis methods will be increasingly used for the more numerous routine determinations such as spectrophotometry, volumetric analysis, gas chromatography, emission spectroscopy and non-destructive neutron-activation analysis. For the larger physicochemical instruments, direct-linked processing of data will increasingly replace hand calculation methods or isolated computer processing.

PRESENT TRENDS

It is interesting to summarize the present trends in various fields of chemical analysis.

Classical wet methods

Progress with automation is not likely to be spectacular. With sufficient numbers of samples some of the operations can be automated. Examples are dissolution of samples, solvent extraction and the separation of ion-exchange and chromatography fractions. A typical approach was the automatic dissolution of metal samples described by Barabas.[20] The metal in the form of a rod is dissolved by anodic dissolution, a graphite rod being used as the cathode. When such an operation is followed for example by spectrophotometry, the complete chemical analysis can be automated.

A wide variety of volumetric and titrimetric analysis methods has been fully described by Squirrell.[11] There are still many possibilities for development or applications which may repay examination by large industrial laboratories.

Spectrophotometry

Ultraviolet, visible and infrared spectrophotometry are included under this heading. Semi-automatic spectrophotometers capable of handling many similar samples are now commonplace in the larger laboratories. The main advantage of such systems is that actual measurement of samples and print-out of results can be obtained while the operator is dissolving samples, or otherwise preparing for the next run. This is well illustrated in the recent developments in automatic clinical chemical analysis of liquid samples such as blood.[1,2,21]

Spectrofluorimetry

For spectrofluorimetry and atomic-fluorescence spectrometry the over-all considerations are similar to those mentioned for spectrophotometry. Perhaps greater care is required for the automation of these determinations. For example, many factors influence the automatic fluorimetric determination of uranium.[3] The automatic spectrofluorimetry of organic compounds is now receiving some attention.[22–25]

Emission spectrometry

Flame spectrometry and atomic absorption are included under this heading. Automatic emission spectrometers are already well-developed and in extensive use. The larger instruments can have 30 or more analytical channels connected to various read-out, print-out or computer systems. Computer processing of data is finding extensive application in this field. The way is now also open for extensive automation of atomic-absorption spectroscopy following the development of simple thermal type resonance monochromators and high-efficiency hollow-cathode lamps.[26,27] Automatic flame spectrophotometry has been in use for some years and there appear to be few difficulties.[28]

X-ray fluorescence spectrometry

Electron microprobe analysis is also included under this heading. Shelemin[3] described three automatic X-ray fluorescence spectrometers developed in 1960–1963. These instruments have now been considerably improved,[29] but the preparation of the necessary solid, powder or liquid sample and placement in the automatic sample changer is still largely manual. The major improvements centre on the programming of variables such as tube voltage and current, crystal, 2θ setting, collimator, detector, counting parameters and method of presentation of results. As with several other instrumental methods, the trend is to couple the output of the X-ray fluorescence spectrometer with a small digital computer[17] which may in turn be linked to a large central computer. The more recent developments in this field have been described by Campbell.[30] A typical modern commercial version[29] will perform determinations of up to seven elements, above atomic number 11, in each sample, allow presetting of three programmes for different types of substances, and offer choice of measuring method (absolute, ratio or vacuum), manual or automatic changing of up to 9 or 160 samples at a time with vacuum air lock, and facilities for computer operation.

Mass spectrometry

Automatic mass spectrometers which can be used for process control or be linked to automatic gas chromatographs, are now well-known.[3,31] Following the introduction of small inexpensive mass spectrometers[32] and computers[17] rapid developments can be expected in their applications for process control. However, in the laboratory the introduction of fully automatic mass spectrometers is not likely to be rapid. Many of these laboratory instruments are required to be versatile and at present this is more easily achieved by manual sample handling. Considerable advances are, however, being made in the application of digital computers[17] for real-time data reduction of mass spectrometer output. There are, consequently, rapidly increasing applications of computers for signal averaging, analysis of cracking patterns, and structure-searching in mass spectrometry.[31]

Nuclear magnetic resonance spectrometry

Potentially, NMR spectrometry can be applied to a useful range of quantitative determinations. Examples are the quantitative determination of hydrogen and fluorine in organic compounds.[33] Similarly, NMR spectrometry can be applied to a smaller range of inorganic determinations. Developments over the next few years are more likely to concern the application of computer techniques for data reduction and improved precision, rather than the automation of NMR spectrometry for plant control. The automation of NMR spectrometers for continuous analysis is briefly discussed by Shelemin.[3] There are also increasing applications in the petroleum industry. In the laboratory the use of integrator technique coupled with curve smoothing could dramatically improve the sensitivity of NMR spectrometers.[34] Recent computer applications in NMR spectrometry have also been reviewed by Lustig.[35]

Electrochemical analysis

The great majority of electroanalytical methods can be automated and numerous applications are detailed in recent reviews.[36] Electrochemical analysis is well suited to automation because many electrical parameters can be precisely measured or are readily available as signals. However, many analytical chemists are not at present very enthusiastic about the automation of certain electrochemical methods such as polarography. Great care is required for the proper functioning of polarographic cells and electrode systems and many chemists therefore consider that manual handling is essential for most laboratory applications. Automated polarography is discussed by Lento.[37] The basis of a simple system is a flow-cell similar to that described by Blaedel and Strohl,[38] incorporated in a commercial autoanalyser system.[9] It is shown that there are very few difficulties in the automatic polarographic determination of cadmium, zinc, lead, magnesium and ascorbic acid.[37] Polarography is typical of a wide range of electrochemical methods and increasing applications can be expected.

Chromatography

Many kinds of chromatography (including gas, paper, column, ion-exchange and ring-oven), have been automated and rapid developments can be expected in the future.[1–3,39–41] A typical automatic gas chromatograph is described by Baker and Orr.[42] The basis of many automatic gas chromatographs is the cyclic cam timer but there are certain difficulties in setting up and adjustment. Increasing attention is therefore being paid to alternative timer or programming systems. Other recent examples of automatic chromatography are gel chromatography,[43] column chromatography[44] and ion-exchange chromatography.[45]

Radiochemical analysis

Automatic radiochemical analysers based on neutron activation, isotope dilution, radiometric titration and precipitation owe much of their origin to the atomic energy industry and are very well documented. McGowan and Foreman[4] give a very good review of on-line analytical instrumentation of nuclear fuel reprocessing plants up to mid-1964. However, this review is not recent enough to deal with the remarkable development and applications of autoanalysers using highly accurate micro-metering pumps based on the peristaltic principle,[9,15] or the more recent applications of computer-coupled instrumentation.[46] Shelemin[3] gave a valuable review of European practice for automatic radiochemical analysis. This review includes details of automatic uranium and plutonium analysers, gamma-absorptiometers, gamma-spectrometers, alpha- and beta-monitors, neutron-monitors, mass spectrometers and a range of automatic counters. Interesting developments in the use of radioisotope sources for X-ray spectrometry[47,48] and for gamma-absorptiometry,[49] also offer promise for a wide range of automatic analysis. There are numerous descriptions of automatic instrumentation and "rabbit" systems for activation analysis with both fast and thermal neutrons, using neutron generators and reactors.[46,50] Perhaps one of the most ambitious schemes for automatic computer-coupled activation analysis was that initiated several years ago by Wainerdi and his school at the A & M College, Texas.[51] These expensive automated systems can only be justified for handling from several hundred to several thousand samples per day. Since the original developmental work was carried out on specially selected fairly pure compounds, the applications to wide varieties of "as-received" samples with variable matrices, are still some years away.

Miscellaneous applications

The reader is referred to the proceedings of recent symposia[1,2] for applications in the following fields: pharmaceutical industry, foods and beverages, agricultural chemistry, power station chemistry, pollution and water analysis, clinical chemistry, biochemistry, immunology, haematology, serology, enzyme research and metallurgical analysis.

CONCLUSIONS

The aim of this review is to provide a general cover of automation in the broad field of analytical chemistry, rather than specific information for the specialist in each subsidiary field. Specialists are undoubtedly aware of many trends towards automation in their own fields.

It seems likely that applications of automation in the average industrial laboratory during the next five years will be confined to the more numerous routine determinations and that the flexibility of manual work will be retained for up to about 20 determinations of a particular type per day.

The greatest effects in the research laboratory will centre around the major items of physico-chemical instrumentation producing a large number of results. Computer processing using direct-coupled (small and large) computers will greatly speed research studies. Under the circumstances, it may be too much to expect the present day chemistry graduate to cope with all aspects of the instrumentation-computer complex. It is true that the analytical chemist could become reasonably proficient in basic electronics, instrument engineering and in applied mathematics, in addition to his chemistry speciality. However, it would appear that a major instrument or group of instruments would provide a maximum return when used to full capacity by a team comprising one or more chemists, an instrument or electronics engineer and a mathematician. In view of the appreciable capital cost of the instrumentation-computer complex for chemical analysis, it is obvious that the more usual operation of an instrument for approximately eight hours per day will be replaced by continuous operation.

Zusammenfassung—Die genenwärtigen und zukünftigen Entwicklungen und Einflüsse von Analysenautomaten und Datenverarbeitungsmaschinen in der analytischen Chemie werden kritisch gewürdigt. Schnelle Entwicklungen konnen bei der Verarbeitung chemischer Routineanalysen und bei der Ermittlung von Daten aus physikalish-chemischen Meßgeräten erwartet werden.

Résumé—On évalue de manière critique les développements présents et futurs et les influences des autoanalyseurs et des appareils de traitement des données en chimie analytique. On peut attendre des développements rapides dans le traitement des analyses chimiques de routins et dans l'évaluation des données de l'instrumentation physico-chimique.

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AUTOMATIC ANALYSIS WITH THERMOMETRIC DETECTION

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Summary—The construction of a cell and associated Wheatstone bridge detector circuitry is described for a thermometric detector suitable for attachment to a Technicon Autoanalyzer. The detector produces a d.c. mV signal linearly proportional to the concentration (0·005–0·1*M*) of the thermally reactive component in the sample stream when it is mixed in the cell with the reagent stream. The influence of various pertinent parameters such as ambient temperature, thermistor voltage, heats of reaction and sensitivity are discussed together with interference effects arising through chemistry, ionic strength effects and heat of dilution.

THE use of the heat of reaction as an inherent and general purpose end-point indicator for titrimetric analysis has long been recognized,[1] but advances in the use of this technique were limited by the relative crudeness of the methods available for following temperature changes. In the last 15 years there has been a great upsurge of interest in this field, because of the availability of thermistors[2] and the means for the continuous recording of data[3] which has resulted in increased accuracy, sensitivity and speed of response. Recent papers describe applications as diverse as the determination of hydroxyl values,[4] titration of basic nitrogen compounds,[5] silicate rock analysis,[6] ionic strength effects,[7] and continuous flow enthalpimetry.[8]

The applicability of thermometric detection to such a wide variety of analytical problems makes it attractive as an adjunct to automatic analysis systems and the present work is concerned with various aspects of this.

EXPERIMENTAL

Apparatus

The apparatus was constructed according to the block diagram in Fig. 1.

Sampling. Three methods of sampling were tried. For laboratory application the Technicon automatic sampler was used. This sampler held 40 samples and a timing disc was cut to give an analysis rate of 20 samples/hr with a sample:blank time-ratio of 1:1.

For simulated on-line applications a pneumatic liquid sampling value was coupled to the sample and the blank streams. This value contained a slider fitted with three drilled holes each with an internal volume of 10 μl. The slider was mounted between two plates so that adjacent holes were in alignment with two pairs of tube ends on either side. Through opposite ends flowed a blank stream to the detection cell and a sample stream to waste or recycle. The first of two electronic timers activated a compressed air valve after a preset delay period and moved the slider so that the bore of the sample tube came into alignment with the two tube ends carrying the blank stream. Simultaneously the second electronic timer was activated. By this means a small discrete quantity of sample was introduced into the blank stream and eventually travelled down into the cell. The second electronic timer held the slider in the injection position for a short delay period at the end of which the slider was restored to its original position, the first electronic timer activated and the cycle repeated. With this technique a series of spikes was recorded that resulted in a "band-width", the thickness of which was a linear measure of the active component in the sample stream.

A third method of sample introduction was by syringe injection into a blank stream through a self-sealing rubber-ended T-piece. This method, so far, has proved to be relatively inaccurate but an approximate estimation of sample strength can be achieved very quickly on very small amounts of sample. Manual syringe injection methods are subject to operator errors but good design can remove much of the error that arises in this application.

Pump. The Technicon peristaltic pump was used throughout. The model was was restricted to one pumping speed.

Flow systems. Individual flow systems were tailored to the requirements of each particular analysis and were designed by standard Autoanalyzer procedures. A basic feature of all flow systems for this detection technique is that they are combined to produce two main streams into the detection cell, a sample stream and a reagent stream. On mixing, the thermal reaction or process renders the sample zone hot or cold relative to the ambient temperature of the heat sink. In order to maintain good zone definition it is necessary to segment the sample stream with air bubbles. This is not necessary with the reagent stream as its composition is held constant. The bubbles in the sample stream must be removed before it enters the cell, otherwise the noise level on the detector is too large. Zone definition is also dependent on flow-rate. Generally the higher the flow-rate the better the definition but there is an upper practical limit set by the capacity of the pump and the inconvenience of using large quantities of reagents and solvents. In practice it has been found that flow-rates through the cell of between 5 and 10 ml/min can give good results, with 8 ml/min as a useful compromise.

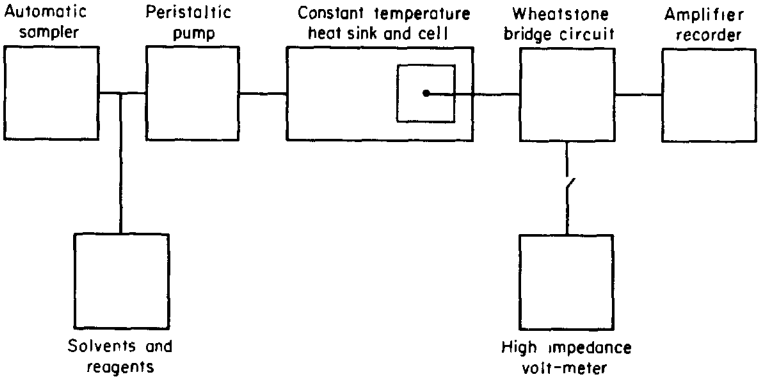


Fig. 1.—Block diagram of apparatus components.

Constant temperature heat-sink. The changes in temperature occurring within the cell are usually very small and it is essential to maintain a constant ambient temperature. In the apparatus described the heat-sink was not thermostatically controlled as it was thought that control to within 0·01° would result in an unsteady base-line when external heat was suddenly injected into the system from the thermostat heater. Instead a 20-l. water-jacket, lagged with polyurethane board was used. In this research, the ambient bath-temperature was manually controlled between runs. Clearly this would be unsatisfactory for on-line control applications and it would be better to fit the heat-sink with a heat-exchange coil through which water is pumped from an external thermostat. The large thermal inertia of the heat-sink would buffer rapid changes in ambient temperature and a steady base-line would result.

Detection cell. The essential requirements of a good detection cell are (*a*) small heat capacity, (*b*) good mixing and (*c*) small internal volume. Various designs have been tried, and though an ideal cell has yet to be constructed the design illustrated in Fig. 2 gives quite satisfactory results. Earlier attempts to construct a cell incorporating a mechanical stirrer were discontinued when it was found that the stirrer was a source of heat input to the system. For simplicity of design and construction, mixing by induced turbulence has many advantages [requirements (*a*) and (*c*)]. To achieve good mixing it requires the sample and reagent streams to be forced through a constriction at high velocity and this results in a build-up of pressure against which the pump must work. Thus it is necessary to check, and to take precautions against, back-flow in some of the pump channels.

Detector circuitry. Circuit details are shown in Fig. 3. Resistances R_1, R_2, R_3, R_4 were put on to long leads and immersed in the heat-sink within a watertight compartment. This ensured reproducible settings and minimized drift. Thermistors, of the type listed in Fig. 3, provided ideal detection elements as regards sensitivity, size and shape. The out-of-balance signal from the Wheatstone bridge was placed across a resistance and condenser in parallel to reduce noise. The potential developed across this resistance was recorded on a Honeywell 1-mV strip chart recorder. The sensitivity of the circuit to cell-temperature changes was controlled by varying the voltage across the cell

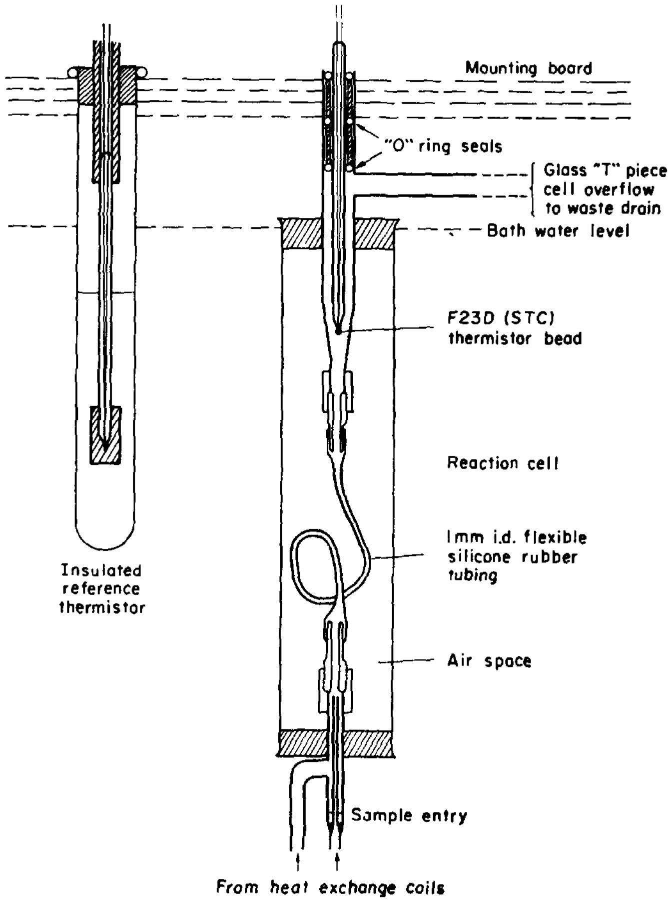


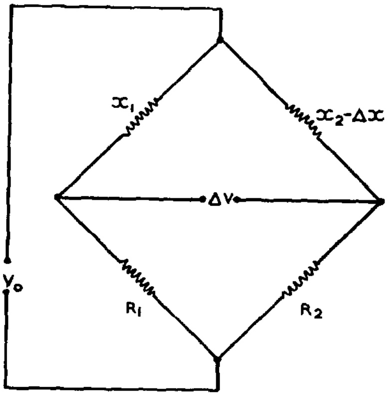
FIG. 2.—Detection cell for continuous thermometric titrimetry.

thermistor. Sensitivity could be increased only until power dissipation in the thermistor bead rose to a level where self-heating resulted in excessive noise. For 2-kΩ thermistors this started to occur above 0·5 V. The response of the circuit was rapid. A high-impedance voltmeter was constructed according to the circuit described by Barry[9] but elaborated to include various voltage ranges.

RESULTS AND DISCUSSION

Detector response to temperature and temperature change

In the circuit



where x_1 and x_2 are matched thermistors, R_1 and R_2 are matched temperature-insensitive resistances and V_0 is the applied voltage across the bridge, the voltages across x_1 and x_2 are

$$V_{x_1} = \frac{x_1}{x_1 + R_1} \cdot V_0 \tag{1}$$

$$V_{x_2} = \frac{x_2}{x_2 + R_2} \cdot V_0 \tag{2}$$

and

$$V_{x_1} = V_{x_2} \tag{3}$$

$$\Delta V = 0. \tag{4}$$

The effects of temperature on x and R are different. While R may, in practice, be assumed constant, the resistance of x alters rapidly with temperature according to the equation[10]

$$x = Ae^{B/T}. \tag{5}$$

Typical values are shown in Table I.

Thus for any ambient temperature T°K the voltage across the thermistor will be

$$V_{x_2} = \frac{Ae^{B/T}}{Ae^{B/T} + R_2} \cdot V_0. \tag{6}$$

The rate of change of voltage with temperature at an ambient temperature of T°K is then

$$\frac{dV_{x_2}}{dT} = \frac{-BR_2}{T^2(Ae^{B/T} + R_2)} \cdot V_{x_2} \tag{7}$$

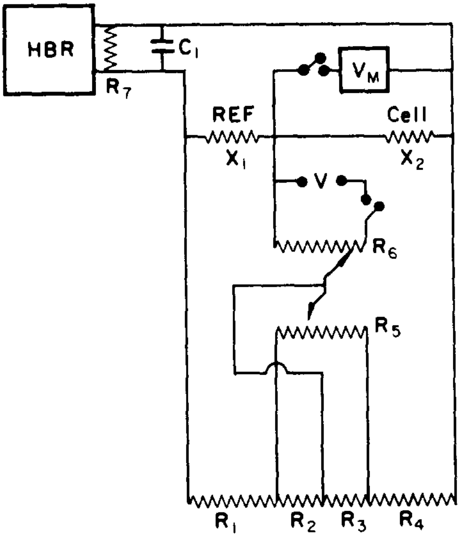


Fig. 3.—Detector circuit details.

R_1, R_4—27 kΩ; R_2, R_3—1·5 kΩ (all at constant temperature in heat-sink). R_5—25 kΩ (10 turn); R_6—10 kΩ (10 turn); R_7—25 kΩ. X_1, X_2—STC F23D thermistors (2 kΩ). V_M—high-impedance voltmeter. V 9-V PP9 dry battery. C_1—500 μF. HBR 1-mV Honeywell-Brown recorder.

TABLE I.—VARIATION OF RESISTANCE WITH TEMPERATURE FOR AN S.T.C. F23D THERMISTOR

x, Ω	$\log_{10} x$	$T - 273$ °K	$\frac{1000}{T}$
3270	3·515	9·15	3·544
3140	3·497	10·25	3·531
2980	3·474	11·60	3·514
2800	3·448	13·25	3·494
2610	3·417	15·00	3·471
2455	3·390	16·75	3·450
2285	3·360	18·75	3·426
2100	3·322	71·10	3·400
1940	3·288	23·35	3·373

$x = Ae^{B/T}$; $A = 0{\cdot}0671$; $B = 3046$.

or

$$\Delta V_{x_2} = \left[\frac{-BR_2}{T^2(Ae^{B/T} + R_2)}\right] . V_{x2} . \Delta T \tag{8}$$

or

$$\Delta V_{x_2} = K_T . V_{x_2} \Delta T. \tag{9}$$

Now ΔV_{x_2} is the out-of-balance voltage produced by a temperature change of ΔT within the detection cell. The signal measured on the recorder, $\Delta\theta$ mm, is also the out-of-balance signal.

Thus $K_1 \Delta\theta = \Delta V_{x_2}$ (K_1 is a constant, in V/mm). (10)

The change in temperature, ΔT, of the flow through the cell is

$$\Delta T = CF_0 . \Delta H . [C_p . F_F . d_F + C_p'] . E \tag{11}$$

where C = concentration of reactive species in sample line to cell (mole/l.)
F_0 = flow-rate of sample line to cell (l./min)
ΔH = heat of reaction (kcal/mole)
C_p = specific heat of cell outflow (kcal/kg/°K)
F_F = flow-rate out of cell (l./min)
d_F = density of flow out of cell (kg/l.)
C_p' = heat capacity of cell (kcal/°K)
E = cell efficiency factor (*i.e.*, degree of mixing, heat transfer, *etc.*)

Then

$$K_1 \Delta\theta = K_T . V_{x_2} . CF_0 . \Delta H[C_p . F_F . d_F . + C_p'] . E \tag{12}$$

or for a standardized flow and analysis system:

$$\Delta\theta = K_T^* C . V . \Delta H_T \tag{13}$$

where K_T^* is the "cell constant" and evaluated by calibration with a standard reaction, at the required ambient temperature, T, thermistor voltage, V, and interpolated heat of reaction, ΔH_T. Equation (13) has been checked experimentally and found to be valid, as the results for the neutralization of sodium hydroxide with hydrochloric acid show: for hydrochloric acid concentrations of 0·0050, 0·0100, 0·0150, 0·0200 and 0·0250M $\Delta\theta$ was found to be 22·7, 44·2, 66·7, 89·0 and 111·1 mm respectively. A linear relationship was also found between $\Delta\theta$ and the thermistor voltage at constant sample strength, heat of reaction and temperature: for values of $\Delta\theta$, in arbitrary units, of 10·4, 20·2, 29·9, 38·6 and 47·7 the corresponding values of V were 0·062, 0·119, 0·173, 0·225 and 0·280 V. For 0·061M solutions the heat of reaction of the neutralization of hydrochloric acid with sodium hydroxide and the reaction of silver nitrate with sodium chloride are −13·7,[11–16] and −15·7 kcal/mole[17] and the values of $\Delta\theta$ 13·7 and 15·7 respectively.

The cell constant was measured over a range of temperatures (Table II).

TABLE II.—VALUES OF K_T*, K_T, ΔH AT VARIOUS TEMPERATURES FOR THE CALIBRATION OF A DETECTION CELL WITH THE REACTION $HCl + NaOH \xrightarrow{\Delta H} H_2O + NaCl$

$T - 273°K$	K_T*	K_T	ΔH, *kcal/mole*
7·9	−124·6	0·03455	−14·21[3]
10·9	−125·2	0·03410	−14·06
15·1	−124·4	0·03360	−13·85
18·5	−123·5	0·03315	−13·78
21·5	−123·4	0·03275	−13·53
25·8	−122·7	0·03210	−13·32
28·7	123·3	0·03180	−13·17
31·6	−123·7	0·03120	−13·02

For this particular cell the constant K_T* turned out to be virtually constant over the temperature range explored. On further examination it would appear that the cell efficiency function, E, may contain a term involving the fluidity of the flow stream through the cell. This may be connected with the degree of mixing attained but has not been fully investigated.

In the simplified equation (12) it is important to recognize the effect of a change in ambient temperature on the voltage across the thermistor. With a rise in ambient temperature the thermistor resistance drops and the proportion of the applied bridge potential across the thermistor also drops (see Fig. 3); in the apparatus described a temperature rise from 20° to 21° resulted in a decrease of 3·5% in the thermistor voltage, with the same decrease in signal. Thus to ensure a ±1% error the ambient temperature had to be held to within ±0·3°. This is rather a limitation on the technique but it can be largely overcome by using a twin thermistor cell and a four-thermistor bridge (see below) or, more simply, by rearranging the circuit in Fig. 3 so that the bridge voltage falls across the two thermistors in series and the out-of-balance signal is taken from the points originally supplied with the bridge voltage.

Heat of reaction and interferences

Like the majority of analytical techniques continuous thermometric titrimetry is subject to interferences. Temperature is one of these and has already been discussed in relation to apparatus performance. The heat of reaction is the physical property that gives rise to this method and is worth examining, not only for interference in a chemical reaction but as a tool for analysis. In continuous flow systems the heat changes detected in the cell are the sum of all the heat change processes occurring and care must be exercised in designing analytical methods.

Effects which give rise to interference in a required chemical reaction are (*a*) temperature, (*b*) ionic strength and chemistry, and (*c*) heat of mixing or dilution.

Temperature. The thermodynamic equation $\Delta H = \Delta G - T\Delta S$ must be taken into account when analysing at an ambient temperature different from that used for calibrating the instrument. The magnitude of this effect is illustrated in Table II. An application is the determination of ΔG and ΔS.

Ionic strength and chemistry. The ionic strength effect on the heat of precipitation of silver halides in dilute aqueous systems has been reported by Ewing and Mazac[1] who found that

$$\Delta H_{\text{obs}} = \Delta H_{\mu=0}(1 + K\sqrt{\mu}) \tag{14}$$

where μ is the ionic strength, and K is a constant.

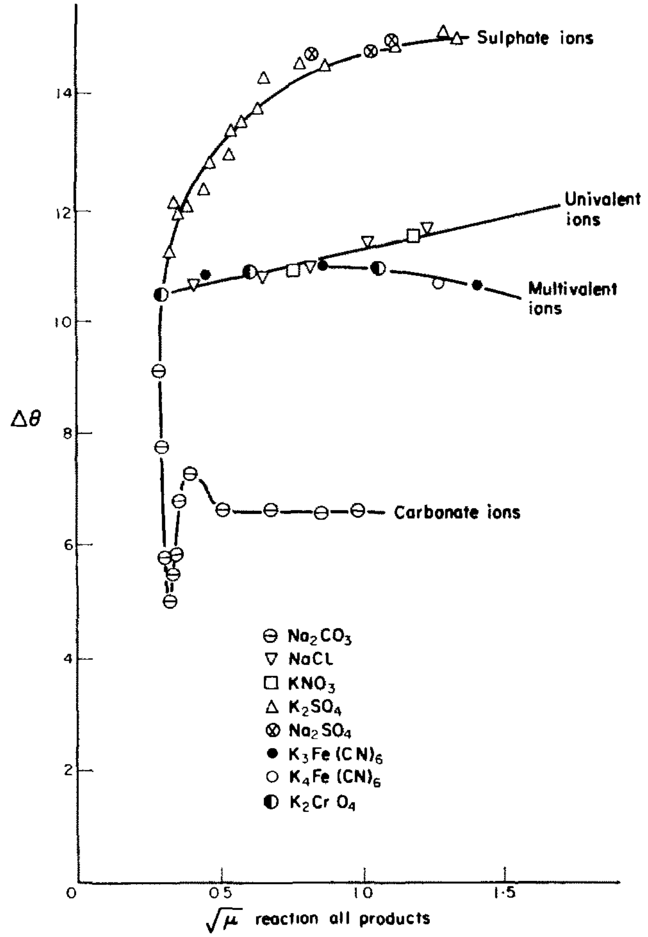


FIG. 4.—Miscellaneous "ionic strength effects" on the continuous thermometric titration of 0·10*M* HCl with NaOH.

Experiments on the reaction between hydrochloric acid and sodium hydroxide would seem to indicate that ionic strength effects are not quite so simple at higher concentration levels. Results shown in Fig. 4 indicate three different kinds of behaviour. One, due to sulphate ions, gave a much enhanced sensitivity. A second, due to carbonate ions, gave a much diminished sensitivity. Presumably the first and certainly the second would involve a change in the final thermal reaction occurring in the cell, and would be largely a chemical effect rather than an ionic strength effect. A third form, due to ionic complexes of transition metals gave only a small effect and was presumably due to ionic strength effects. The effect of multivalent ions appears different from that of univalent ions.

Two other forms of chemical interference have also been observed in connection with precipitation reactions. In the determination of sulphate ions through the precipitation of barium sulphate the nucleation and release of the heat of precipitation is subject to a variable delay or induction period. As a result the reaction zone may have passed the detector before any heat is released and by then it is too late for it to be registered. The induction period increases as the concentration of sulphate decreases. A partial reduction of the induction period can be made by having a constant bleed of sulphate ions into the sample stream diluent. The second form of interference was noted during a prolonged run of chloride, bromide and iodide determinations with silver nitrate reagent. Sensitivity gradually increased and this was attributed to changing heat-transfer properties of the glass coating around the thermistor bead due to an increasing deposit of silver halide.

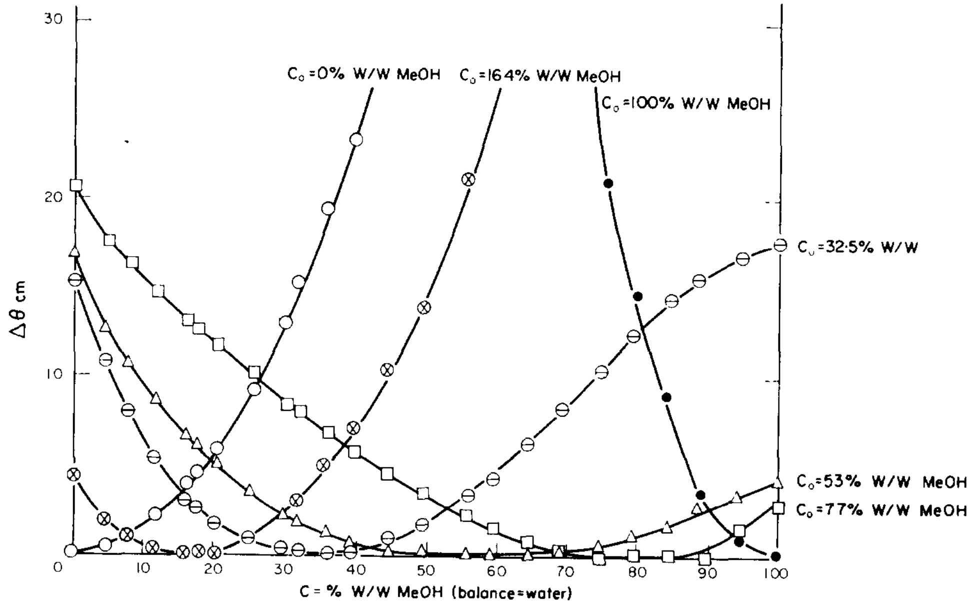


FIG. 5.—Detector response to the heat of mixing for the binary system methanol-water. C = sample composition; C_0 = diluent composition.

Heat of mixing. In a continuous-flow system this effect cannot be separated from the heat of chemical reaction, as it can be, on kinetic grounds, with the conventional slow addition of reagent to a stirred sample in a Dewar flask. The heat change occurring on mixing can be either endothermic or exothermic and its magnitude quite large. In this phenomenon the relationship between temperature change and concentration is peculiar in that a rough empirical rule is

$$\Delta\theta = f(C - C_0)^2 \tag{15}$$

where C is the concentration of the component to be diluted in the sample stream and C_0 is the concentration of the same component in the reagent stream. Experimental values of $\Delta\theta$ *vs.* C (methanol–water samples) and for varying values of C_0 (methanol–water "reagent") are shown in Fig. 5 for the entire binary system. Such an analytical system has the bizarre feature that the sample is titrated with the component to be determined (*e.g.*, titration of methanol–water mixtures with water to determine water). The rough general equation (15) can be used to provide a very sensitive and simple method for detecting small changes in binary composition over narrow intermediate ranges and should have many useful applications. The empirical rule is also applicable to aqueous solutions of most inorganic salts.

When the heat of dilution is an interference effect its relative effect on the heat of reaction can be much diminished by operating at a greater dilution of the sample, *e.g.*, with a 10-fold dilution of a sample before loading the sampler the heat of dilution is reduced to 1% [*i.e.*, $(1/10)^2$] of the original, while the heat of reaction has been reduced to 10% of its original value. This aspect provides a good argument for operating at low concentrations with very sensitive detectors.

Precision of analysis

The apparatus described is essentially for laboratory use and not for long-term on-line applications. As such it is capable of good precision, Table III. The sampling rate in Table III was 30/hr and while the precision is good the relationship of $\Delta\theta$ *vs.* [HCl] is slightly non-linear. This is believed to be due to the time allowed becoming increasingly insufficient for the same steady-state to be attained as, the acid content of the samples increased. With a slower rate of sampling (20/hr) this effect was not observed.

TABLE III.—REPEATABILITY TESTS FOR THE CONTINUOUS THERMOMETRIC TITRATIONS OF HYDROCHLORIC ACID SAMPLES WITH SODIUM HYDROXIDE REAGENT OVER AN 8-HR PERIOD

HCl, *M*	0·010	0·025	0·050	0·075	0·100	0·125	0·150
Mean value $\frac{\Delta\theta}{n} = \overline{\Delta\theta}$ $(n = 28)$	1·46	3·77	7·62	11·07	14·50	17·63	20·77
Mean deviation $= \frac{\Sigma\lvert\overline{\Delta\theta} - \Delta\theta\rvert}{n}$	0·049	0·070	0·063	0·105	0·146	0·155	0·189
Std. devn. $= \sqrt{\frac{\Sigma(\overline{\Delta\theta} - \Delta\theta)^2}{n - 1}}$	0·063	0·087	0·109	0·130	0·199	0·237	0·306

Simulated on-line analysis with the pneumatic liquid sampling valve over an 8-hr run on a 1*M* hydrochloric acid sample gave the results summarized in Fig. 6. Again precision is quite good. A slight downward drift of $\Delta\theta$ at either end of the run is closely followed by a drift in the ambient temperature of the heat-sink. This demonstrates the effect of changes in ambient temperature.

The precision so far obtained with manual syringe injection techniques was seldom better than ±5% relative.

Sensitivity

With the apparatus described and a flow-system where the sample intake is 10–20% of the total flow through the cell, a useful working range for the active component in the samples is 0·005–0·10*M*. For a (2-kΩ) thermistor voltage of 0·3 V a full scale deflection of 1 mV corresponded to approximately 0·1°.

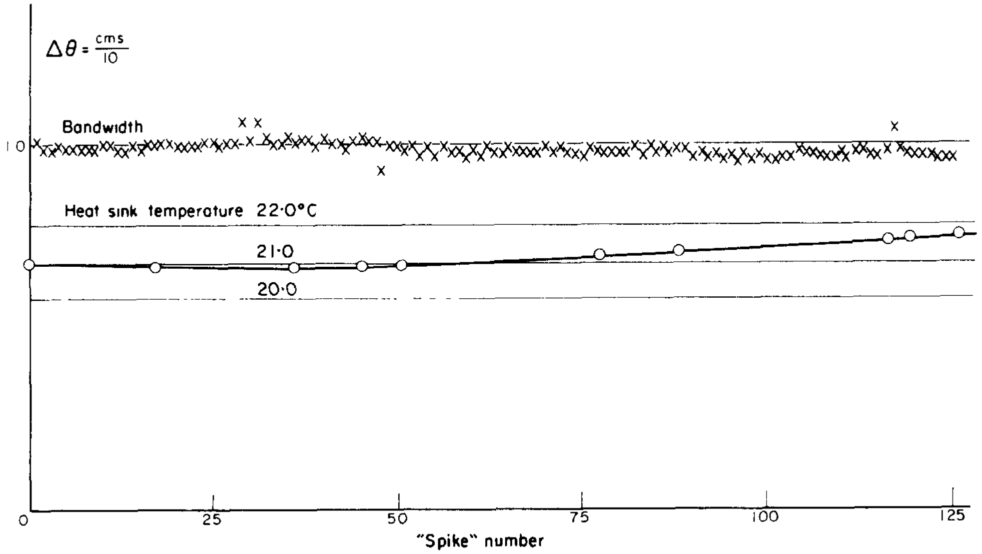


Fig. 6.—Band-width and temperature drift on a simulated on-line analysis of 1·0*M* HCl, with a 10-μl pneumatic sampling valve.

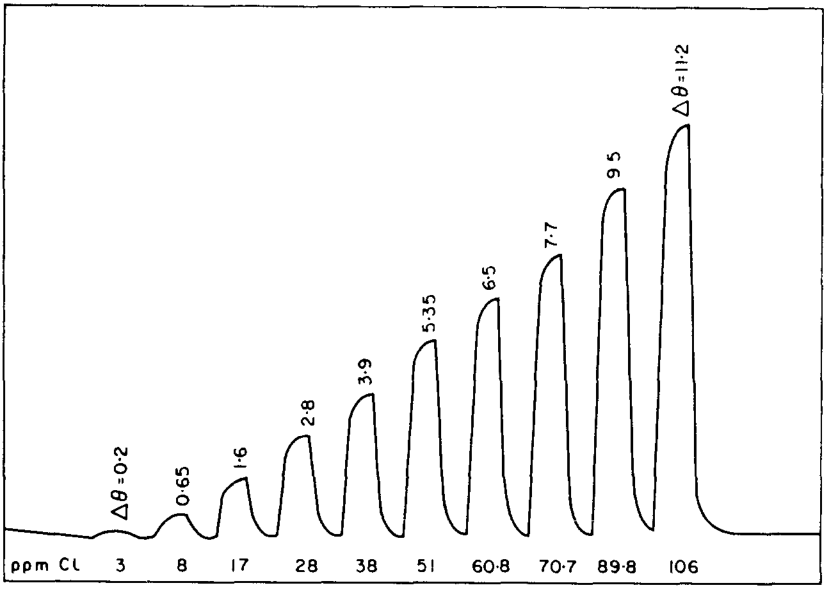


Fig. 7.—Continuous thermometric determination of chloride. Calibration recorded for range 0–100 ppm.

Higher sensitivities can be achieved, at least in theory, by modifying the Wheatstone bridge to use a twin thermistor cell with thermistors of a higher resistance, or by use of alternative and novel methods of narrow-span resistance measurements. With the use of a novel and experimental a.c. bridge circuit it was possible to detect ppm concentrations of chloride, see Fig. 7, and extend the possible applications of this method to the determination of chloride in raw water supplies. With manual syringe injection techniques as little as 2 μg of chloride could produce a definite observable signal.

CONCLUSIONS

The results of this work confirm the findings of Sebborn *et al.*[2] that continuous-flow thermometric titrimetry is a feasible technique that, with good design, lends itself to accurate analysis. However, as with most quantitative methods of analysis its usefulness is limited by certain boundaries. These are summarized below.

Applications	*Restrictions in quantitative analysis*
Acid-base titrations	Temperature
Redox titrations	Thermistor voltage
Complex formation titrations	Interference effects through more than one thermal process
Precipitation titrations	Lower limits of detection
Heats of reaction	Quality and performance of equipment
Heats of dilution	
Ionic strength effects	
Thermodynamic parameters (ΔG, ΔS *etc.*)	

As well as apparatus design and performance one of the main objects of this work has been to examine and explore the various restrictions on this technique. Clearly the most important practical analytical aspect is the design of a flow system of sample, solvent and reagent that results in isolation of the required reaction from any interference effect and to cause it to occur in the cell. As already mentioned this is best done by operating at high dilution with very sensitive detectors. It seems that this is now the direction to proceed with further work.

To obtain increased sensitivity there appear, at least in theory, to be some advantages in operating with a four-thermistor bridge with a twin-thermistor cell. By having opposite bridge thermistors in the cell the out-of-balance effect from one pair is added to that of the other and an immediate doubling of sensitivity is achieved. At the same time the problem of maintaining a constant thermistor voltage is made easier. Also, as the calculations below will show, there are sensitivity advantages to be obtained by operating with higher resistance thermistors at higher voltages. The relationship applicable to a single thermistor cell, equation (7), with V replacing V_{x_2} now becomes, for a twin thermistor cell

$$\frac{1}{2}\cdot\frac{\mathrm{d}V}{\mathrm{d}T}=\frac{-B(Ae^{B/T})\,.\,V}{T^2[(Ae^{B/T}+Ae^{B/T})]} \tag{16}$$

or

$$\frac{\mathrm{d}V}{\mathrm{d}T}\sim\frac{-BV}{T^2} \tag{17}$$

Since the voltage across the thermistors can only be raised to the level at which the power dissipation starts to introduce excessive noise, then a higher sensitivity should be obtained with a higher voltage across the thermistors of a higher resistance. If it is assumed that the thermistors are all loaded to a common maximum power dissipation of $W_{\max}$ where $W_{\max} = V^2_{\max}/R$, then

$$\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{\max} = \frac{-B.\sqrt{W_{\max}.R}}{T^2}. \tag{18}$$

The following table indicates on a relative basis the maximum theoretical sensitivities of double and single thermistor cells, with different STC F-type thermistors.

Table IV.—Maximum sensitivities, at equal power dissipation, on a relative basis for single and double thermistor detection cells

Thermistor type (STC)	Resistance, R, $k\Omega$	B	$V_{\max}$ *Volts*	$(dV/dT)_{\max}$ = rel. max. sensitivity	
				single	double
F 15 D	100	4000	3·53	0·500	1·000
F 14 D	10	3400	1·12	0·135	0·269
F 33 D	5	3250	0·79	0·091	0·182
F 23 D	2	3050	0·50	0·054	0·108
F 22 D	0·2	2500	0·16	0·014	0·028

This table suggests that a 20-fold improvement in sensitivity could be obtained for a double thermistor (100 kΩ) cell as against the present single thermistor (2 kΩ) cell. Such an improvement in sensitivity would greatly enhance the usefulness of the technique by extending the working range down into the ppm range. At these levels its sensitivity would be approaching that of colorimetric methods of analysis.

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Zusammenfassung—Die Konstruktion einer Zelle und einer Wheatstone-Brückenschaltung für einen zum Anschluß an einen Technicon-Autoanalyser geeigneten thermometrischen Detektor wird beschrieben. Der Detektor liefert ein Gleichspannungssignal im mV-Bereich, das der Konzentration (0,005–0,1M) der thermisch reaktiven Komponente im Probenstrom linear proportional ist, wenn der Probenstrom in der Zelle mit dem Reagens-Strom gemsicht wird. Der Einfluß verschiedener einschlägiger Parameter wie Umgebungstemperatur, Thermistorspannung, Reaktionswärmen und Empfindlichkeit werden zusammen mit Störeffekten diskutiert, die aus chemischen Eigenschaften, Einflüssen der Ionenstärke und Verdünnungswärmen resultieren.

Résumé—On décrit la construction d'une cellule et d'un circuit détecteur en pont de Wheatstone associé pour un détecteur thermométrique convenant comme accessoire à un Autoanalyseur Technicon. Le détecteur produit un signal en courant continu mV linéairement proportionnel à la concentration (0,005–0,1*M*) en constituant thermiquement réactif dans le courant d'échantillon lorsqu'il est mélangé dans la cellule avec le courant de réactif. On discute de l'influence de divers paramètres correspondants comme la température ambiante, le voltage du thermistor, les chaleurs de réaction et la sensibilité en même temps que des influences gênantes provenant de la chimie, des effets de force ionique et de la chaleur de dilution.

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POTENTIALITIES OF INFRARED SPECTROSCOPY IN DETERMINING TRACES OF CARBON OR OXYGEN AS CARBON DIOXIDE

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Summary—The determination of traces of carbon dioxide by infrared spectroscopy has been investigated. For maximum sensitivity the absorption band at 2350 cm^{-1} is measured, the total pressure being raised to one atmosphere by addition of an inert gas. With a micro gas-cell and a beam-condenser the limit of detection is 0·02 μg of carbon, and for 4 μg of carbon the coefficient of variation is 1·5%.

IN THE determination of traces of oxygen by the inert-gas fusion method, carbon monoxide is produced and may be measured directly. More commonly, the carbon monoxide is converted into carbon dioxide which is separated in a freeze-trap and measured manometrically.[1] Similar measurements of carbon dioxide are employed in the determination of traces of carbon by the combustion method.

The manometric technique has proved satisfactory for as little as 10 μg of carbon or oxygen, but it is difficult to construct a combined freeze-trap and gauge with a volume smaller than 0·5 ml, and for lower weights of the elements an alternative method of measuring the oxides of carbon was considered desirable. The results of an investigation into infrared spectroscopy are presented below; the potentialities of several other techniques have also been examined, and these will be compared in a subsequent publication.[2]

Gases which have molecules composed of just a few atoms have relatively simple infrared spectra, and the bands are often specific in experiments involving mixtures. This specificity is of course assured if a single absorbing gas is mixed with non-absorbing gases such as monatomic or symmetrical diatomic species.

The intensity–concentration relationships do not necessarily follow the Lambert-Beer law. Deviations are found, particularly among gases of low molecular weight, and are due in part to collision-broadening of the rotational fine structure of the bands. Broadening can be caused by the addition of an inert gas, and an effect commonly observed at low spectrometer resolution is a marked enhancement of the intensity of a band envelope as the pressure of inert gas is increased.[3] This effect is of analytical value.

The relative absorption intensities of many gases have been indicated in the literature.[4] Carbon dioxide has a more intense absorption than carbon monoxide by virtue of the band at 2350 cm^{-1}, and this gas was therefore selected for study. Weaker bands are to be found at 3720, 3610 and 670 cm^{-1}.

Collision-broadening effects are observed in carbon dioxide at relatively low pressures, and useful intensity enhancement factors can be obtained by raising the pressure of the system to one atmosphere with inert gas. It is convenient to use nitrogen or air for this purpose. Complete broadening of the rotational structure of carbon monoxide is only achieved at pressures of many atmospheres;[5] this is due to the wider spacing of the rotational lines, consequent on the smaller moment of inertia of the molecule.

EXPERIMENTAL

Apparatus

Perkin-Elmer model 137G grating near infrared spectrophotometer.

Experiments with a standard 10-cm gas cell

The gas was contained in a 10-cm path-length cylindrical pyrex cell with entrance and exit ports. The spectrophotometer was open to the air and spectra were run with the standard slit programme.

Streams of carbon dioxide and nitrogen from two cylinders were mixed and passed into the cell, and the flow-rates, which were shown to be reasonably constant, were measured at the exit port with a soap-bubble flow-meter. The system was assumed to be at atmospheric pressure, and the partial pressure of carbon dioxide was thus given by:

$$P_{CO_2} = \frac{CO_2 \text{ flow-rate}}{(CO_2 + N_2) \text{ flow-rate}} \times \text{atmospheric pressure.}$$

The weight of carbon (or oxygen) corresponding to the amount of carbon dioxide in the cell could thus be calculated; in the results which follow, only weights of carbon are given. Care was taken to

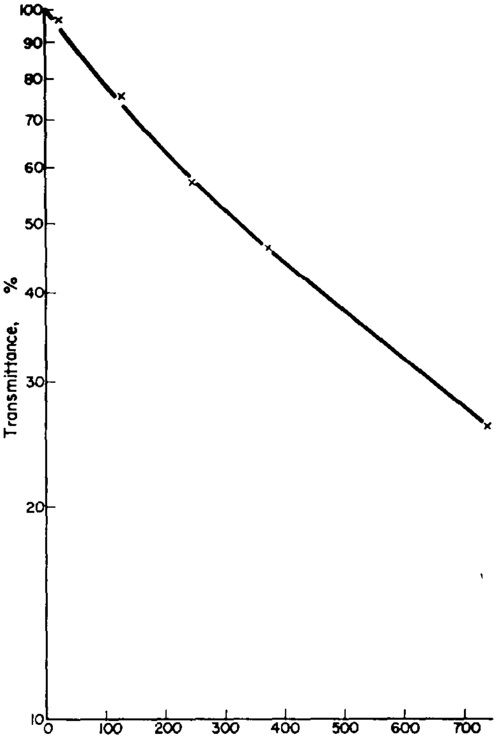

FIG. 1.—Determination of carbon dioxide in admixture with nitrogen at a total pressure of one atmosphere, using a standard 10-cm gas cell.

ensure adequate purging of the cell at each level of concentration. The cell was sealed off and a spectrum recorded; a compensation cell in the reference beam was filled with nitrogen.

Results. The fine structure of the bands was not observed; only the envelopes could be seen. The maximum absorptions of the bands at 3720 cm^{-1} and 2350 cm^{-1} were determined as the carbon content of the cell was varied from 23 mg down to 21 μg (290 to 0·27 mm Hg pressure of carbon dioxide). The results for the 2350 cm^{-1} band are shown in Fig. 1 as a semi-log of transmittance *vs.* weight of carbon in the cell.

Experiments using a micro gas-cell

The use of a cylindrical gas cell is wasteful, and if the quantity of gas available is small, it can be measured more efficiently in a minimum-volume cell with dimensions tailored to those of the spectrophotometer beam. The absorbance of a given quantity of gas increases as shorter cells are used; the reduction in path-length is more than compensated for by the increase in pressure because of the tapered construction of the cells. The efficiency is increased still further if a beam-condenser is used to concentrate the light from the source on to the sample contained in a very small volume.

A micro gas-cell, with a path-length of 8 mm and a volume of 0·15 ml, was used in conjunction with a beam-condenser fitted with potassium bromide lenses. The transmission of light through the cell was about 60% and a wire gauze attenuator was placed in the reference beam.

The cell was attached to a vacuum line and carbon dioxide was admitted at various pressures. The absorption was measured, and again after admission of air to raise the pressure to atmospheric. In the latter case it was necessary to allow about 10 min for complete mixing of the gases within the cell, the absorption then being seen to reach a maximum.

The sensitivity of the measurement was improved by increasing the slit width, and thus the available energy, this giving a more accurate pen response; it was further improved by purging the spectrophotometer with nitrogen to reduce absorption by atmospheric carbon dioxide.

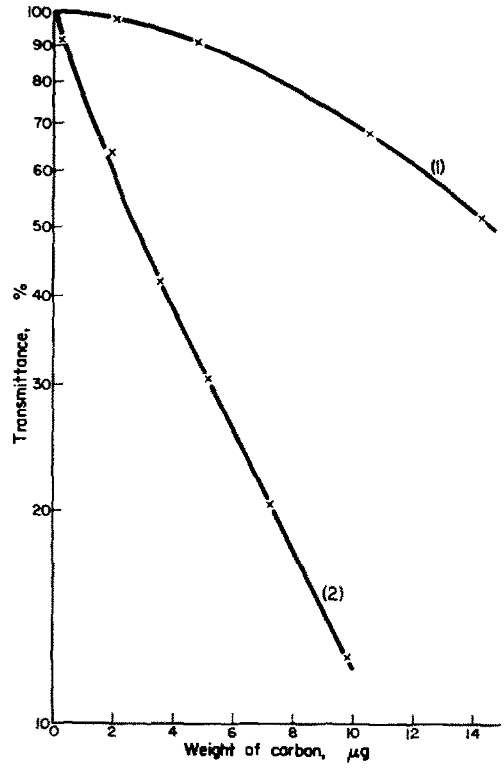

Fig. 2.—Determination of carbon dioxide, using a micro gas-cell and beam-condenser. (1) carbon dioxide alone; (2) carbon dioxide mixed with air at a total pressure of one atmosphere.

Results. The maximum absorption of the band at 2350 cm^{-1} was determined as the carbon content of the cell was varied from 9·8 μg down to 0·26 μg (93 to 2·5 mm Hg pressure of carbon dioxide). The results are shown in Fig. 2.

The reproducibility was assessed by measuring the absorption when the micro-cell was repeatedly filled with a carbon dioxide/nitrogen mixture from a flowing gas stream of constant composition. At the 40% transmittance level, which corresponds to 4 μg of carbon, the coefficient of variation was 1·5% (10 readings).

The limit of detection was about 0·02 μg of carbon. This was taken as $2\sqrt{2} \times$ the standard deviation of the blank, which was measured with the cell filled with air (10 readings).

DISCUSSION

The standard 10-cm gas cell could conveniently be used to determine quantities of carbon in the 10–750 μg range, by measuring the band at 2350 cm^{-1}. It would be possible to extend the measurements to significantly higher weights of carbon by using the band at 3720 cm^{-1}; here the peak absorption was only 5% of that at 2350 cm^{-1}, and with 20 mg of carbon in the cell the transmittance was still 20%. The calibration curve for this band is not illustrated, but is similar in form to that shown in Fig. 1.

A micro gas-cell and beam-condenser enabled the 0–10 μg range to be studied, and the limit of detection was 0.02 μg of carbon. Lower limits could doubtless be achieved if ordinate expansion, greater source energy and better purging facilities were available.

With a given sample it would be important to introduce as much as possible of the carbon dioxide into the cell in order to achieve the high sensitivity of which the method is capable. A convenient experimental assembly might embody a Toepler pumping system by which the same fraction of gas could be transferred in each determination.

No effects were observed which could be attributed specifically to adsorption of carbon dioxide on the cell walls. Any such effects may be minimized by mixing the carbon dioxide with the inert gas before admission to the cell,[6] or by coating the metal surfaces of the cell with a suitable varnish.[5]

The large difference between the curves for carbon dioxide alone and carbon dioxide in admixture with air (Fig. 2) may be attributed to pressure broadening effects. Although the latter curve is almost linear, the former shows a progressive intensification of the absorption as the pressure of gas is increased. No previous report of this effect has been found for carbon dioxide, although it has been observed in nitrous oxide at low pressures;[7] some theoretical justification for it has also been presented.[3]

The method is rapid; once the cell has been filled with gas it is a simple matter to position it in the spectrophotometer and to scan through the 2350 cm^{-1} band. Care must be taken, however, to minimize any unwanted changes in absorption due to temperature and pressure fluctuations, and to introduce the carbon dioxide reproducibly into the cell.

A recent method for the determination of traces of acetylene, carbon monoxide and nitrous oxide[8] used a versatile spectrophotometer equipped with ordinate expansion. The gas was contained in a 1-metre cell. Such long path-length cells are well suited to the study of trace concentrations of gases in mixtures where the sample volume is not limited, as for example, in the field of air pollution. If the trace constituent can readily be separated then a method at least as sensitive can be achieved by the use of a micro gas-cell and beam-condenser.

Acknowledgement—We are grateful to Research and Industrial Instruments Company Ltd. for the loan of a micro gas-cell and beam-condenser.

Zusammenfassung—Die Bestimmung von Kohlendioxidspuren durch Infrarotspektroskopie wurde untersucht. Für maximale Empfindlichkeit wird die Bande bei 2350 cm^{-1} gemessen, wobei durch Zugabe von Inertgas der Gesamtdruck auf eine Atmosphäre gebracht wird. Mit einer Mikro-Gasküvette und einem Strahlkondensor ist die Nachweisgrenze 0,02 μg Kohlenstoff, bei 4 μg Kohlenstoff der Variationskoeffizient 1,5%.

Résumé—On a étudié la détermination de traces de gaz carbonique par spectroscopie infra-rouge. Pour la sensibilité maximale, on mesure la bande d'absorption à 2350 cm^{-1}, la pression totale étant élevée à une atmosphère par addition d'un gaz inerte. Avec une microcellule à gaz et un condenseur de faisceau, la limite de détection est de 0,02 μg de carbone, et pour 4 μg de carbone le coefficient de variation est de 1,5%.

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AN X-RAY MILLIPROBE ANALYSER WITH PHOTOGRAPHIC RECORDING OF THE SPATIAL DISTRIBUTION OF ELEMENTS

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Summary—An X-ray milliprobe analyser has been built and its performance and usefulness evaluated. The instrument consists of a fluorescent X-ray spectrometer in which the primary X-ray beam from the sealed-off tube is collimated so that only a small area on the specimen, 0·3 or 1 mm in diameter, is irradiated. The large loss in intensity of the fluorescent X-rays is offset to some extent by the use of a focussing curved-crystal analyser. The usefulness of the instrument has been greatly increased by the incorporation of an automatic raster scanning motion in the sample holder, and of a similar motion in a colour-film holder which moves across a light beam. The colour of this beam is altered according to the measured concentration of the element, so that a coloured mosaic picture of its distribution is built up. The limits of detection of a wide range of elements are in the range 200–2000 ppm for the rather short counting period of 10 sec per point which is necessary when scanning a large area.

THE X-ray milliprobe analyser is one of a number of instruments which can be used for the analysis of selected small areas on the surface of a specimen, and the particular features of the instrument which will be described are derived from an attempt to adapt it to those fields of use where it has advantages over other methods. Its main characteristics are as follows.

(*a*) A spatial resolution of 0·3 mm.
(*b*) Limits of detection in the range 200–2000 ppm (10-sec counting times) for a wide range of elements.
(*c*) A wavelength resolution modest compared with that of a conventional fluorescent X-ray spectrometer.
(*d*) The ability to examine non-conductors without further treatment.
(*e*) The exposure of the sample to only a low vacuum (2 mbar)
(*f*) That the cost of the instrument is quite low if it is conceived and used as an attachment to an existing spectrometer which provides the high voltage power supply and the X-ray tube.

These characteristics should be compared with the corresponding properties of the other instruments.

1. The electron microprobe analyser, in which spots about 1 μm in diameter are irradiated in a high vacuum by an electron beam and the resultant X-rays recorded.
2. The laser microprobe analyser, in which a pulsed laser beam is focussed on to the surface of a specimen so that material in a spot about 50 μm in diameter is vaporized into the spark gap of a spark source spectrograph.
3. Charged particle activation methods,[1] in which spots 25 μm in diameter are irradiated with high energy protons, deuterons or helium ions, and the scattered particles or the γ-rays from induced nuclear reactions are measured.

It is apparent that the poor spatial resolution of the X-ray milliprobe makes it quite unsuitable for the examination of microscale inclusions and inhomogeneities in fine-grained materials, as is often required in metallurgical problems. The electron microprobe analyser is the obvious choice in this field, whilst the laser microprobe is an alternative should difficulties arise, since it operates at atmospheric pressure and is unaffected by the conductivity of the sample. Charged-particle methods, though they use expensive accelerators, can have a high sensitivity for certain elements (especially the light elements) which the other methods lack. The milliprobe is, however, useful in the examination of larger inclusions, especially in natural minerals and ores, and it is in precisely such circumstances that a conventional X-ray fluorescence spectrometer is likely to be available already. The high spatial resolution of the other methods may be an embarrassment in such circumstances, as in the absence of rapid scanning attachments it may not be possible to average out variations within the inclusions.

Every method of examining a small selected area is potentially one of mapping the two-dimensional distribution of an element over a larger surface, however, and all that is required is some means of altering the relative position of sample and beam. The extent to which the incident beam of radiation may be scanned over the surface of a stationary specimen is limited in the electron and laser microprobes by off-axis aberrations in the focussed incident beam, and by the lower resolution which must be tolerated in their focussing radiation analysers in order to allow the radiation source to be moved away from the focal point. Mulvey[2] found in the case of a 250-mm radius focussing curved crystal analyser used in an electron microprobe that the permissible shift of the electron beam was only 10 μm for a high resolution quartz crystal and 100 μm when a lithium fluoride crystal was used. By sacrificing some resolution in the analyser, Duncombe[3] was able to scan an area of 400 × 400 μm before the lens aberrations in his electron microprobe analyser became the limiting factor. In the X-ray milliprobe analyser it is inconvenient to alter the direction of the collimated X-ray beam at all. Thus it is necessary to have some automatic method of moving the specimen. In the case of the microprobe analysers there is the further problem that the high spatial resolution can become an embarrassment in that the scanning of a finite area requires a very long time, as an adequate number of photons have to be collected at each point, and will produce an overwhelming amount of data (an area 10 × 10 mm contains 10^8 1-μm squares). Clearly it is undesirable to attempt to examine finite areas at such high resolution, and although the spatial resolution of a microprobe may be degraded to give an average reading over a larger area, either by defocussing the electron beam (the laser beam must be kept focussed to produce the heating necessary for vapourization) or by averaging the results from a 400 × 400 μm scan, it is more economic to use a cheaper instrument with an inherently lower spatial and spectral resolution, like the milliprobe, whenever areas more than 1 mm square are to be examined.

Apart from the examination of macroscale inclusions in minerals, and of small (mm size) specimens such as thin wires, the main field of use of the milliprobe then appears to be in the examination of quite large areas (10 × 10 mm) of specimens for inhomogeneity on the macroscale, as in the examination of small castings, and diffusion boundaries in welds and brazes. With this in mind the instrument was designed to incorporate a sample stage which could be driven stepwise in the X and Y directions, and, as some means of dealing with the mass of data produced, a photographic recorder in which a colour film pack is moved synchronously across a beam of light. The colour of this beam of light is changed by rotating filters to correspond to the concentration of the element being measured, and a coloured concentration distribution is produced.

DESIGN OF X-RAY MILLIPROBES

Conventional spectrometers can be modified as milliprobe analysers by removing the Soller slit system and substituting a pinhole very close to the specimen surface to define the point being analysed, and a slit roughly in the position of one of those at the crystal end of the Soller slits.[4,5] If the distance between pinhole and slit and the slit dimensions are chosen to give the same divergence of the secondary X-ray beam, both in the plane of diffraction and at right angles to it, as when a Soller slit is used, then the fluorescence intensity is reduced by roughly the same factor as the reduction in the area of the sample seen by the crystal, that is, probably by a factor of 100–200. This loss of intensity can be mitigated by using a curved crystal as a wavelength analyser since this is capable of accepting a much more divergent beam of radiation providing that it is divergent from a point or line source. This is exactly the case when a small area of the sample is being examined, and Miller[5] was able to improve the sensitivity of the Norelco instrument with pinhole attachment by a factor of six in this way. He increased the width of the slit so that the divergence of the secondary beam in the plane of diffraction was increased from about 0·5° to 6°, and focussed the radiation with a curved analysing crystal.

The possibility of using a curved-crystal spectrometer accepting a beam of divergent radiation introduces a futher choice into the design of a milliprobe, since it is possible to define the spot being examined either by masking the beam of secondary radiation leaving the sample, as was done by Miller, or by collimating the primary beam of X-rays falling onto the sample. An attempt has been made to use a beam of primary X-rays focussed to a point by an auxiliary curved-crystal spectrometer,[6] but there was an unacceptable loss of intensity due mainly to the fact that the spectrometer made the beam monochromatic as well as focussed, so that most of the radiation in the primary continuum was lost.

Collimating the primary X-ray beam has the advantage that the radiation intensity in the vicinity of the sample is quite low so that the irradiation area can be viewed indirectly by a microscope, and this is the method used in the instrument to be described, as well as in those of Adler and Axelrod[7] and Thatcher and Campbell.[8] The design of the primary X-ray collimator is a compromise between intensity and convenience. For the highest intensity of primary radiation falling on the selected area it is important to ensure that it sees *via* the collimator the whole of the anode area of the X-ray tube which is generating X-rays. In the case of a spectrographic tube this may be a projected area 13 mm in diameter, so that the collimator would become a conical mask with a pinhole at its tip. The beam leaving this would be highly divergent and the tip would have to be placed very close to the specimen surface to keep the irradiated area not much larger than the pinhole aperture. A tubular collimator, by producing a more parallel beam, allows a greater distance between the tip of the collimator and the sample surface and facilitates the viewing of the specimen. It does this, however, at the expense of reducing the anode area seen by the irradiated spot, and if the tube is made too long the sensitivity could be appreciably less than in the alternative system used by Miller.

The fundamental equations of curved-crystal X-ray optics are illustrated in Fig. 1. The fully focussing Johansson arrangement is shown in which the analysing crystal is bent to a cylindrical radius $2R$ and then has its inner surface ground to a radius R. The Bragg condition, $n\lambda = 2d \sin \theta$ still holds for this crystal, but the result of bending and grinding is that radiation divergent from a source at any point on the focussing circle radius R (the Rowland circle) is brought to a focus at another point on the circle if $l = 2R \sin \theta$, where θ is the angle of incidence to a tangent to the circle at the centre of the crystal, and l is the source-to-crystal distance. Combining these two equations gives the basic relationship for curved-crystal spectrometers

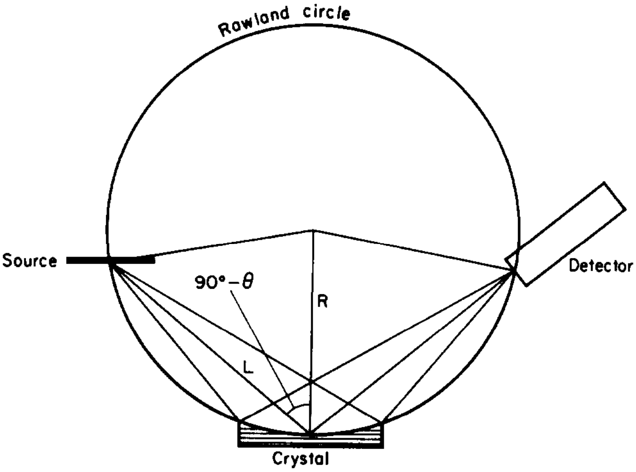

FIG. 1.—Curved-crystals optics.

$$l = \frac{Rn\lambda}{d} \tag{1}$$

The resolving power of any X-ray spectrometer of which the resolution is not limited by the line-broadening effect of the crystal may be obtained by differentiating Bragg's equation and eliminating d to give

$$\frac{\lambda}{\mathrm{d}\lambda} = \frac{\tan \theta}{\mathrm{d}\theta} \tag{2}$$

In the case of a flat-crystal instrument $\mathrm{d}\theta$ is the divergence of the beam leaving the Soller slit system, whilst for a curved crystal-instrument $\mathrm{d}\theta$ represents the difference in the angle of incidence of rays coming from the extremities of the sample spot and is defined by the sample width at right angles to the line of take-off of radiation; if this is x, $\mathrm{d}\theta = x/l$,

and
$$\frac{\lambda}{\mathrm{d}\lambda} = \frac{2R}{x} \tan \theta \sin \theta \tag{3}$$

The function of the goniometer mechanism in a curved-crystal spectrometer is different from that in a conventional spectrometer. Assuming that the area being examined is kept as a stationary point on the Rowland circle, the function of the goniometer is to move both the crystal and the detector round the circumference of the Rowland circle, the detector at twice the angular velocity of the crystal. Adler and Axelrod, and Thatcher and Campbell, used conventional goniometer mechanisms. It is implicit in such mechanisms that not only the sample spot but also the centre of the Rowland circle (*i.e.*, the axis of the goniometer) is fixed in space. In the spectrometer designed by Adler and Axelrod the sample surface was in a plane tangential to the Rowland circle and at right-angles to the plane of the circle. As a consequence, the take-off angle (the angle at which X-rays must leave the sample to strike the centre of the crystal) varied with the position of the crystal. Such an arrangement is to be avoided if possible, since the variation in angle may give rise to additional variations in the sensitivity from one element to another, and to variations in the effect of surface finish. The change in take-off angle alters the projected size of the sample spot at right angles to the take-off line, and in this case helps to compensate for the deterioration in resolution which otherwise occurs at small values of θ. Thatcher and Campbell arranged the plane of the sample face to be nearly in the plane of the goniometer, and thus produced a more complicated situation as well as limiting the take-off angle which could be used.

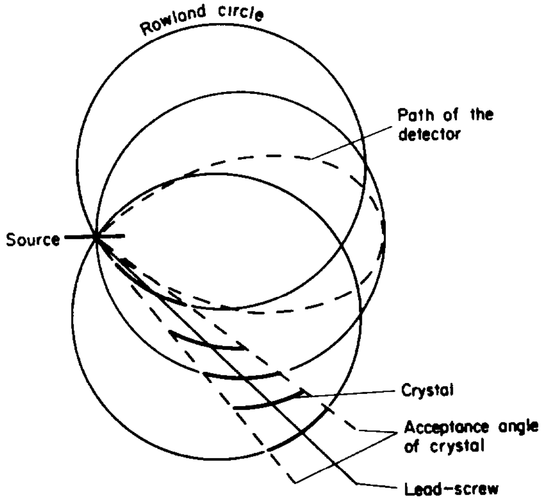

FIG. 2.—Motions of crystal and detector.

Our present instrument and its earlier prototype[9] follow the Applied Research Laboratory instruments[3] in that the take-off angle is kept constant by pivoting the crystal on a guide which is driven along a lead-screw set at a constant angle to the face of the specimen. The Rowland circle must now move in space, pivoting about the sample spot, the crystal acting as if it were a cam bearing against the circumference of the hypothetical circle. The detector moves in a more complicated clover leaf path with the source at one apex. These motions are illustrated in Fig. 2. The instrument to be described differs from the A.R.L. models in that the motion is achieved by a simple linked rod mechanism due to Barstad and Refsdal.[10] The original mechanism was designed to operate with the centre of the Rowland circle and the crystal as fixed points, but it was easily adapted to the present purpose. A third way of producing the correct motion with a constant take-off angle has been described recently.[11]

EXPERIMENTAL

The present X-ray milliprobe is an automated version of the prototype analyser described at the Society for Analytical Chemistry Conference at Nottingham in 1965.[9] The general arrangement of the X-ray tube, sample carrier, goniometer and detector is shown in Fig. 3. The specimen is put face down over a 40 × 60 mm aperture in the sample holder. The sample holder itself is carried on an arm attached to carriages which are driven in the X and Y directions by stepping motors, the arm allowing this mechanism to be clear of the X-ray tube. The sample is irradiated from below by a 1-kW Philips X-ray tube (tungsten target) fitted with interchangeable tubular collimators such that the primary radiation strikes the sample at an angle of 45°. The lead-screw for the crystal is also set at an angle of 45° to the sample surface and is driven by a stepping motor. The rod linkage mechanism of the goniometer is shown in detail in Fig. 3. The central part of the mechanism is the bar carrying the crystal mounted at right-angles to it. This bar always lies along a radius of the Rowland circle. At its lower end it is pivoted on a block which moves along the lead-screw. At its upper end it is joined to two radius arms, one pivoted at its remote end opposite the point where the primary X-ray beam strikes the sample, and the other carrying the detector at its remote end. Equal angles between the central arm and two side-arms are maintained by a sliding yoke on the central bar which is linked to the outer arms by short equal rods. The detector is free to turn about the end of its radius arm, and is kept aimed in the right direction by a steel wire and a 2:1 pulley drive. So far xenon-filled proportional counters with 12 × 5 mm apertures have been used as detectors. The spectrometer was designed to have a radius of 100 mm, and a 50 × 25 mm LiF crystal bent to a radius of 200 mm and ground to a radius of 100 mm has been used as the analysing crystal. The area under examination can be viewed *via* four mirrors with a microscope, and the whole spectrometer is mounted inside a vacuum-tight case.

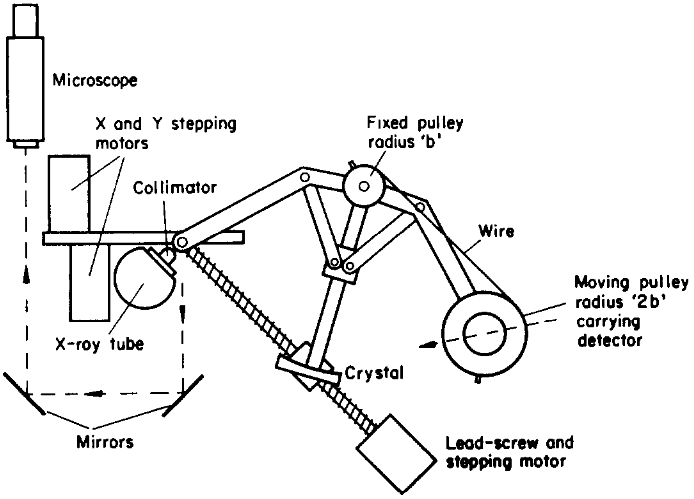

FIG. 3.—Mechanism of the spectrometer (only two mirrors shown).

Pulses from the detector are fed to standard counting equipment (Harwell 2000 series units) including a ratemeter, and the counts collected may be printed out on an Addo-X printer or displayed as a ratemeter trace on a chart recorder. A programming unit has been built for the stepping motor drives. The unit allows the goniometer to be set, *via* the lead-screw and its stepping motor, at up to 30 preselected values of sin θ in turn and the usual continuous scans may also be made. Values of sin θ have been used rather than values of λ as this eliminates resetting of the values whenever the crystal is changed, and because there are already extensive compilations of 2θ values for different elements and analysing crystals. The sin θ readings are linear in both λ and rotation of the lead-screw, as $\sin\theta = n\lambda/2d = l/2R$. For the LiF crystal, $\lambda = 4{\cdot}027 \sin\theta$. Another part of the programming unit drives the X and Y stepping motors of the sample holder. Either motor may be driven independently to position the sample or to examine a line on its surface. In the scanning mode one motor is driven for a predetermined number of 0·3-or 1-mm steps before the other is moved one step. The first motor is then driven in reverse until another line of the scan has been completed, when the second motor is again moved one step. In this way a raster scan can be performed.

The photographic display of the results of such a scan performed at a fixed wavelength setting is produced by a system similar to that used by Fudge and Causer,[12] and the basic mechanism is shown in Fig. 4. A Polaroid colour-film holder is mounted on a carriage which can be moved in the X and Y directions by stepping motors in synchronism with the movement of the sample. Whenever the analysis of a point on the surface of the sample is completed the corresponding point on the film is illuminated momentarily by a beam of light which passes through a colour filter and a mechanical shutter. The colour filters are in fact ten sectors of a disc rotated by a repeater motor which is in turn driven by the ratemeter. In this way a coloured mosaic photograph of the distribution of an element is built up, the colours representing a tenfold division of the range in use on the ratemeter. By alteration of the ratio of the lengths of the increments in the sample and film holder movements a mechanical magnification or reduction may be achieved.

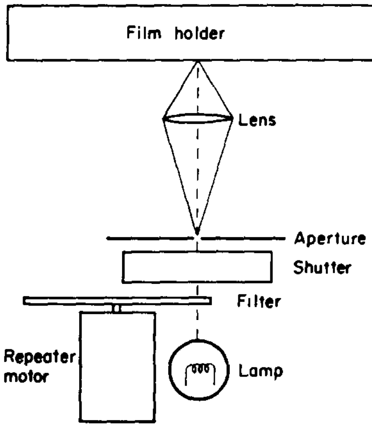

FIG. 4.—Diagram of the camera.

RESULTS AND DISCUSSION

In order to evaluate the performance of the instrument as a spectrometer, measurements were made on pure specimens of most of the elements detectable with the given combination of X-ray tube, crystal and detector. The geometry of the goniometer limited the usable range with the LiF crystal to 0·7–3·6 Å (corresponding to 2θ angles of 20° and 125° on a conventional spectrometer) and this allowed the *K* lines of elements 20–42 and the *L* lines of elements 50–92 to be measured. The X-ray tube was usually run at 40 kV, 20 mA, with a 1-mm diameter collimator, and all the results have been normalized to a power of 1 kW at 40 kV. The errors in the goniometer settings, the count-rates on the lines, the count-rates on the adjacent backgrounds, and the peak half-widths were measured in one series of experiments.

Reproducibility and accuracy of the goniometer

The reproducibility of the goniometer was tested by repeatedly approaching the half peak-height setting (the position where the count rate is half that at the maximum) on a given peak from both directions of travel and observing the difference in the readings. This was usually done for the *K* lines of elements such as scandium at the long-wavelength end of the goniometer setting. Here the peak-width is smallest and the half peak-height setting is at its most sensitive. It was shown that the reproducibility of the setting for either direction of travel alone was better than

1×10^{-4} ($\sin \theta$ value), but that the backlash, the difference between the readings taken in the forward and reverse directions, varied with the condition of the bearings in the pivots of the linkage. With a set of well used, apparently slack, bearings the backlash was about 3×10^{-4}, but this increased to 12×10^{-4} when new tight bearings were fitted. These figures may be compared with those for a conventional goniometer. Here, the reproducibility usually specified, 0·01° of arc, corresponds to uncertainties of $1{\cdot}5 \times 10^{-4}$ in $\sin \theta$ when $2\theta = 60°$, and of $0{\cdot}9 \times 10^{-4}$ when $2\theta = 120°$. Thus a "run-in" rod linkage goniometer is only a factor of two or three worse than the best geared model, and the effects of this uncertainty in angle setting are largely masked by the poorer resolution of the milliprobe at short and medium wavelengths. The absolute accuracy of the goniometer was also measured by comparing the values of $\sin \theta$ at which the maxima of the peaks occurred with the values calculated from the dimensions of the goniometer, the d spacing of the crystal and the wavelength of the lines. The error was on average $+2 \times 10^{-3}$ (observed — calculated) in the region near $\sin \theta = 0{\cdot}9$ ($\lambda \sim 3{\cdot}6$ Å), fell to zero at about $\sin \theta = 0{\cdot}35$ (1·4 Å) and reached -2×10^{-3} at the lower wavelength limit of $\sin \theta = 0{\cdot}177$ (0·71 Å).

Sensitivity

The count-rates for the lines, adjacent backgrounds and the limits of detection are given in Tables I and II. It has been assumed that the photons are counted for a period of only 10 sec, since this is probably the longest time it is possible to dwell on a given selected spot when scanning a large area. The limit of detection is taken to be that concentration (in ppm) which will give a count equal to three times the standard deviation of the background count in the specified time interval. Since the count-rates are measured on pure materials it is implied that the sensitivities will hold for a matrix with a mass absorption coefficient similar to that of the pure material. If only a limited number of points is to be examined then greater sensitivities than those given in the tables can be achieved by increasing the counting time.

The count-rates for the L_α lines are between 1/5 and 1/7 of those for the K_α lines of the same wavelengths, as is expected. The ranges of atomic number covered by the K and L lines do not overlap and there is a region of zero or poor sensitivity between $Z = 43$ and $Z = 59$. This gap could be partially closed if an LiF crystal cut in the 110 plane rather than the 200 plane were used as an alternative. The smaller d spacing of this crystal (1·424 Å) should allow wavelengths down to 0·48 Å to be recorded, and allow measurements on the K_α lines of elements up to tin ($Z = 50$). It is not feasible to redesign the goniometer movement to extend the short wavelength coverage, as the crystal mount is already very close to the sample at the short wavelength limit and the background count-rate tends to rise rapidly at small angles of incidence. Measurements of the elements with atomic numbers lower than that of calcium would require the use of a crystal of larger d spacing (say pentaerythritol, $d = 4{\cdot}371$ Å) and a gas-flow proportional counter. In a conventional X-ray spectrometer a vacuum is necessary in the sample chamber only for the measurement of elements of atomic number lower than that of calcium, and the improvement brought about in the present spectrometer by using a vacuum at wavelengths as short as 1·6 Å reflects the fact that the air-path is longer, and that its length increases as the goniometer is set for longer wavelengths.

The count-rates, as a whole, are about 50 times those recorded with the prototype

TABLE I.—COUNT-RATES AND LIMITS OF DETECTION FOR VARIOUS ELEMENTS—K_α LINES

Atomic number	Element	Wavelength of line, *Å*	Line count-rate, *c/s*	Background rate, *c/s*	Limit of detection, *ppm*
20	Calcium	3·360	2800	13	1200
21	Scandium	3·032	4500	21	950
22	Titanium	2·750	7200	20	580
23	Vanadium	2·505	13000	38	450
24	Chromium	2·291	20000	61	370
25	Manganese	2·103	28000	80	300
26	Iron	1·937	33000	94	280
27	Cobalt	1·790	50000	140	220
28	Nickel	1·659*	56000	140	200
29	Copper	1·542	48000	110	210
30	Zinc	1·437	44000	140	250
32	Germanium	1·341	51000	300	320
33	Arsenic	1·256	45000	450	440
34	Selenium	1·177	49000	450	410
38	Strontium	0·877	49000	600	470
39	Yttrium	0·831	48000	600	480
40	Zirconium	0·788	46000	620	510
41	Niobium	0·748	42000	600	550
42	Molybdenum	0·711	35000	600	660

* Measurements at this and longer wavelengths were made with the spectrometer evacuated to 2 mbar.

TABLE II.—COUNT-RATES AND LIMITS OF DETECTION FOR VARIOUS ELEMENTS—L_α LINES

Atomic number	Element	Wavelength of line, *Å*	Line count-rate, *c/s*	Background rate, *c/s*	Limit of detection, *ppm*
50	Tin	3·600	120	10	25000
51	Antimony	3·439	390	10	7700
52	Tellurium	3·289	500	10	6000
53	Iodine	3·148	520	10	5800
56	Barium	2·775	970	9	2900
57	Lanthanum	2·665	1200	12	2800
58	Cerium	2·561	1800	23	2500
59	Praseodymium	2·463	1450	13	2300
60	Neodymium	2·370	2800	18	1400
62	Samarium	2·199	4500	25	1000
63	Europium	2·121	5500	25	850
64	Gadolinium	2·046	6500	31	810
65	Terbium	1·976	7700	33	710
66	Dysprosium	1·909	8500	37	680
67	Holmium	1·845	9000	50	740
68	Erbium	1·784	9600	57	750
69	Thulium	1·726	8500	61	870
70	Ytterbium	1·672*	9600	63	780
73	Tantalum	1·522	7200	48	920
78	Platinum	1·313	9000	130	1200
79	Gold	1·276	9000	260	1700
82	Lead	1·175	10000	280	1700
83	Bismuth	1·144	10100	330	1700
92	Uranium	0·911	11500	380	1600

* Measurements at this and longer wavelengths were made with the spectrometer evacuated to 2 mbar.

instrument,[9] a difference which might be expected from the increased X-ray tube power, and about 10 times those recorded by Thatcher and Campbell using a 1·75-kW tube. Part of this latter difference can be attributed to the fact that the 50-mm long, 100-mm radius crystal in the present instrument intercepts radiation over an angle of 14° in the plane of the gonimeter, whereas the 75-mm long, 200-mm radius crystal used by Thatcher and Campbell intercepted an angle of 10·5°. The major part of the difference must, however, arise from other causes, and it seems unlikely that it is due to the different take-off angle. The count-rates obtained in the present instrument are comparable with those that might be expected of an instrument of the type described by Miller, making allowance for the different sizes of collimator.

The replacement of the 1-mm diameter collimator by one of diameter 0·3 mm reduces the count-rates by a factor of 30, whilst the use of a 1 × 10 mm slit (with the long axis at right angles to the plane of the goniometer) increases them by a factor of 30. Now the area of the 0·3-mm collimator is 1/11 of that of the 1-mm collimator, and the slit, area 13 times that of the 1-mm collimator, so the extra factors of about three in the intensity changes in each case indicate that the two circular collimators do indeed behave as tubular ones progressively restricting the area of the anode seen by the irradiated spot. Assuming that the line-to-background ratios remain the same, the limits of detection change by factors of $30^{-\frac{1}{2}}$, and it is apparent that the 0·3-mm collimator is of use only in special cases. The reduction of the limit of detection by a factor of 5·5 when the slit is used raises the interesting possibility that the milliprobe might then be sensitive enough to do duty as a conventional large-area spectrometer. The sample would need to be moved with a reciprocating motion in a direction at right-angles to the long axis of the slit so that the reading would be averaged over a large area of the surface. It would be reasonable to assume that the sample could be irradiated for at least 100 sec in this mode, so that the limits of detection might be reduced by factors of up to 20.

Resolving power

The observed half-height widths of the peaks are compared in Fig. 5 with the theoretical widths calculated from equation (3). This equation assumes that the source size is so large that it is the dominating factor in determining the resolution of the instrument. This is to be expected since a 1-mm source is a very large one by electron microprobe standards, and the close fit between the experimental points and the theoretical curve confirms it. Equation (3) gives $d\lambda$, the shift of wavelength represented by rays coming from the extremes of the irradiated area, and this would produce a square-shaped peak if the area were square and uniformly irradiated. When the take-off angle and the angle of incidence of primary radiation are both 45°, the projected image of the area in a plane at right-angles to the take-off line is a circle of the same diameter as the collimator, *i.e.*, 1 mm. This has a half-height width of 0·866 mm and this would be the correct value to use for x were the area evenly illuminated. By making ratemeter readings as a 0·05-mm knife-edge was scanned backwards and forwards across the irradiation position, it was possible to show that the intensity of the primary radiation fell off rapidly towards the edges of the area and that the radiation fell to half its maximum intensity at an apparent projected diameter of 0·59 mm. This was the value used for x in equation (3). The corresponding curves for flat-crystal optics with an LiF crystal with fine (160 μm) and coarse (480 μm)

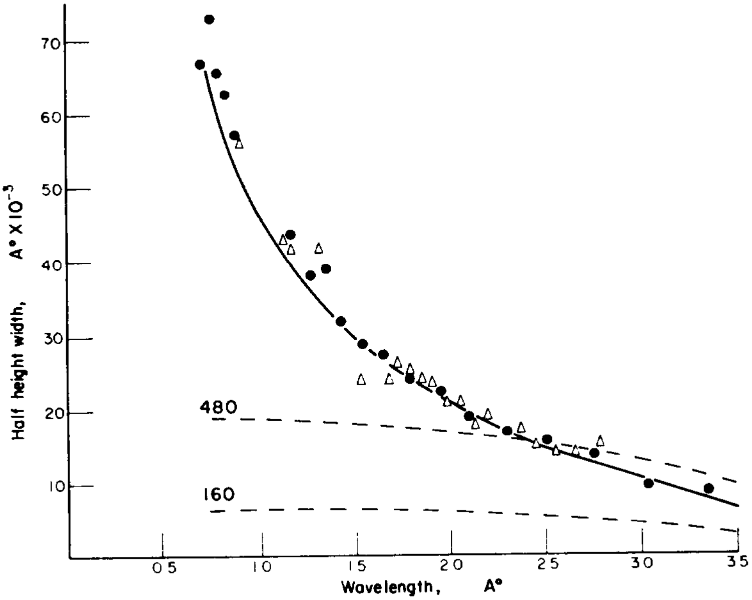

Fig. 5.—Graph of resolution against wavelength.

collimators are included for comparison. It can be seen that the goniometer, the LiF crystal being used, will resolve the *K* lines of adjacent elements in the Periodic Table for $Z = 20$–32, and the L_α lines of adjacent elements for $Z = 50$–69.

The scanning mechanism

This has been used for a considerable period of time and has been shown to be reasonably reliable. The photographs in Fig. 6 are of a test specimen consisting of shallow holes of various sizes in an aluminium square 25 × 25 mm filled in with nickel oxide. The sample-carriage motion was adjusted in this exposure such that it moved only 0·4 mm at each measurement, and the 1-mm irradiated areas therefore overlap. This appears to improve the spatial resolution, probably because the area which is strongly irradiated is less than 1 mm in diameter. As a result the sharp boundaries at the edges of the circles are rendered as a transition involving three points in the mosiac. Allowing a minimum counting time of 10 sec, which implies that the concentration designated as the limit of detection cannot be more than 10% of the full-scale ratemeter reading, and about 2 sec to move to the next position, the instrument cannot examine more than 300 points per hr. For zero overlap on the points this is an area of 300 mm^2 per hr.

CONCLUSION

The instrument has now been in regular use for about four months. In this time it has been used mainly to make scans of relatively large areas of casts of experimental alloys, and this justified the premises on which the design was based. The overall performance, both as regards sensitivity, resolution and the coverage of elements is not as good as that of a conventional spectrometer, but the use of a slit collimator and additional crystals should improve the performance to the point where the instrument might be used in many of the applications of a conventional analyser as well as in its more specialized applications.

Zusammenfassung—Ein Röntgen-Mikroanalysengerät wurde gebaut und seine Arbeitsweise und sein Nutzen getestet. Das Instrument besteht aus einem Röntgenfluoreszenzspektrometer, in dem der primäre Röntgenstrahl aus der abgeschmolzenen Röhre kollimiert wird, so daß nur eine kleine Fläche auf der Probe von 0,3 oder 1 mm Durchmesser getroffen wird. Der große Intensitätsverlust an Röntgenfluoreszenzstrahlung wird teilweise kompensiert durch die Verwendung eines fokussierenden Analysators mit gebogem Kristall. Die Nützlichkeit des Instruments wurde stark erhöt durch Einbau einer automatischen Raster-Bewegungsmöglichkeit im Probenhalter und einer analogen Bewegung in einen Farbfilmhalter, der sich durch einen Lichtstrahl bewegt. Die Farbe dieses Strahls ändert sich entsprechend der gemessenen Konzentration des Elementes, sodaß sich ein Farbmosaik seiner Verteilung bildet. Die Nachweisgrenze für viele Elemente liegt bei 200–2000 ppm bei der recht kurzen Zählperiode von 10 sec pro Punkt, was bei Überstreichen einer großen Fläche notwendig ist.

Résumé—On a construit un analyseur à rayons X "milliprobe" et évalué ses possibilités et son utilité. L'instrument consiste en un spectromètre à fluorescence de rayons X dans lequel le faisceau de rayons X primaire du tube scellé est collimaté de sorte que seulement une petite surface du specimen, de 0,3 ou 1 mm de diamètre, est irradiée. La grande perte en intensité des rayons X de fluorescence est compensée dans une certaine mesure par l'emploi d'un analyseur focalisant à cristal incurvé. L'utilité de l'instrument a été fortement accrue par l'incorporation, dans le porte-échantillon, d'un mouvement automatique d'exploration, et d'un mouvement semblable dans un support de pellicule en couleurs qui se déplace à travers un faisceau de lumière. La couleur de ce faisceau est altérée suivant la concentration mesurée de l'élément, de sorte qu'il s'édifie une image en forme de mosaïque colorée de sa répartition. Les limites de détection d'un grand nombre d'éléments sont dans le domaine 200–2000 p.p.m. pour la période de comptage relativement courte de 10 secondes par point qui est nécessaire lors de l'examen d'une importante surface.

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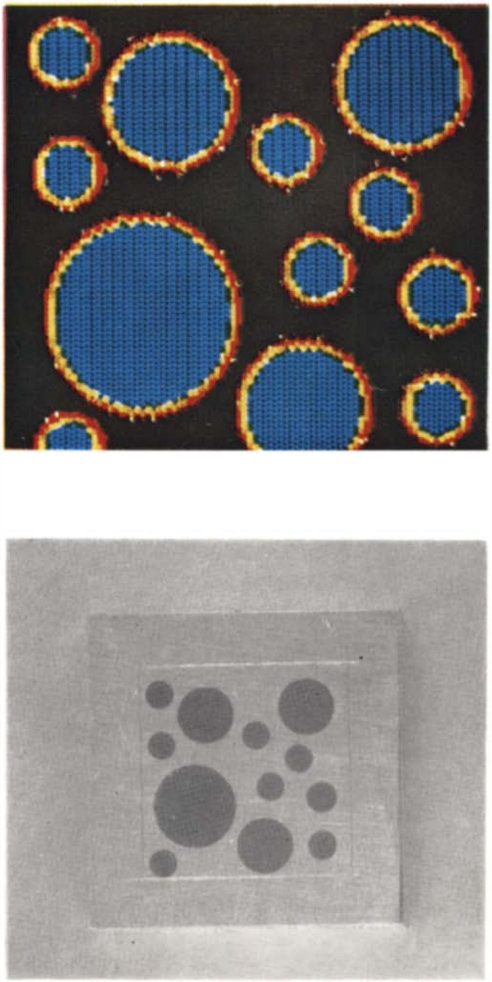

FIG. 6.—Photographs of test piece (lower) and scan for nickel K_α (upper), the latter at magnification of ×2·5.

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SPUTTERING OF GaAs SINGLE CRYSTALS BY 8–16 keV ARGON IONS

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Summary—An apparatus for the measurement of sputtering yields (S) of single crystals of GaAs bombarded by argon ions is described. The dependence of S on target temperature and ion energy and the anisotropic nature of the sputtering at high temperature is discussed.

BECAUSE of the absence of long close-packed atomic chains in the zinc blende structure, and the polar nature of the [111] axis, III–V semiconductors lend themselves to the study of the effect of short-range surface structure on sputtering of regular two-component systems.

Although numerous experimental results have been obtained on the sputtering of elemental semiconductors,[1–6] those available for compound semiconductors are still very limited.[4,5,7,8] In addition, except in isolated cases[6] all of these studies have been made with inert gas ion energies of less than 2 keV. At these energies the majority of bombarding ions penetrate only one or two atomic layers so that the spot patterns formed under these conditions must only involve very short collision chains. Using ion energies below 2 keV, Anderson[4] observed the formation of spot patterns in the sputtered deposit from GaAs when the sample temperature was above 130°. Below this temperature (T_a) the semiconductor surface was permanently damaged by ion bombardment, the surface becoming amorphous after a small radiation dose. Under these conditions the deposit was radially symmetrical and isotropic in composition.

This report describes the measurement of the sputtering yield of GaAs single crystals bombarded by 8-16 keV Argon ions. The effect of temperature on the yield and spot patterns formed is also examined. The anisotropic nature of the sputtering has been studied by neutron-activation analysis of various areas of the sputtered material deposit.

EXPERIMENTAL

Apparatus

The apparatus consisted of a conventional R.F. discharge ion source operating at 30 MHz. The ions were extracted from the source, focussed by an Einzel lens and deflected through 90° by an electrostatic lens of 76 mm mean radius. The sample was mounted on a copper block which was electrically insulated from its supporting stand by mounting it in a silica disc. The temperature of the target was thermostatically regulated by an NiCr/NiAl thermocouple and Transitrol Unit controlling a small heater coil set in the block. The sample crystal was held on the block by a thin nichrome plate with a 5-mm hole in its centre. A schematic diagram of the sample mounting arrangement is shown in Fig. 1. The ion beam diameter at the target was about 2 mm in most experiments but was reduced to 1 mm for studies of spot pattern formation. Secondary electrons from the sample were suppressed by maintaining the sample at +120 V relative to the sample support. Sputtered material was collected on discs of silica or glass placed directly in front of the sample.

The focussing region and sample chamber were each pumped by a trapped and baffled 50-mm mercury diffusion pump. With the ion source input closed the sample chamber pressure was lower than 60 pbar. During a run the pressure rose to 1–2·5 nbar. The current density of the argon beam

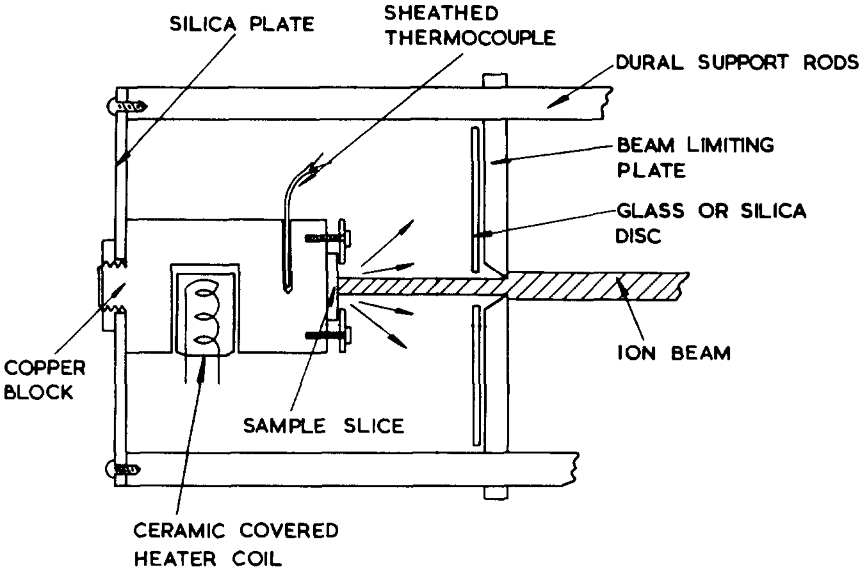

FIG. 1.—Schematic diagram of the sample holder.

at the sample varied from 1·40 μA/mm^2 at 8 keV to 4·00 μA/mm^2 at 16 keV. These intensities were several times greater than the intensity of impurities striking the sample surface and of the same order of magnitude as the residual argon collision intensity. Although the argon ions were not mass-analysed the contribution of Ar^{2+} to the beam in this type of source is expected to be less than 6%.

Materials

The single crystals of GaAs, which were in the form of slices about 1 mm thick, were polished by hand and then lightly etched before washing and weighing. X-Ray diffraction measurements showed that the crystals were aligned along the (111), (110) and (100) planes to better than 3°.

The argon used was taken directly from a storage bottle of high-purity gas. Mass-spectrometric analysis of a sample of the residual gas in the target chamber showed air impurities to be less than 0·1%.

Procedure

The measurement of sputtering yield was carried out as follows. The etched, washed and weighed sample was placed on the copper block and the nichrome retainer carefully fastened down. After the sample and collecting disc were visually aligned with the ion beam axis the sample chamber was replaced and the apparatus pumped down. The sample was then heated to at least 250° for half an hour before being adjusted to the final running temperature. After the undeflected ion beam had settled down it was switched on to the sample. The charge falling on to the sample was measured by integrating the current flowing between the sample and ground. The sample weight difference before and after sputtering was measured on a Mettler M5 microbalance.

RESULTS

Visible effects of temperature on the sputtering of GaAs (110), GaAs (111), GaAs $(\bar{1}\bar{1}\bar{1})$ *and* GaAs (100).

GaAs (110). Between 8 and 16 keV the annealing temperature (T_a) was 125° ± 5°. At temperatures below T_a the sputtered deposit was radially symmetrical and showed no special features for each of the surfaces examined, and at temperatures above T_a spots were formed in the $(\bar{1}11)$, (111), (100) and (010) directions. Several features of the deposits are noteworthy. In general the high-temperature deposit (430°) is more distinct than the low-temperature deposit (300°). At 430° the (111) and $(\bar{1}11)$ spots are different in size, the $(\bar{1}11)$ spot being the larger. The texture of the $(\bar{1}11)$ spot is dull as compared with the bright spots at (100), (010) and (111). Anderson had observed that the $(\bar{1}11)$ spot was thicker than the (111) spot and also slightly dull. The (100) spots are prominent but smaller than the (111). Between the $(\bar{1}11)$ and the (100) spots there is a deposit which must indicate an expansion of the spots along the $(01\bar{1})$ plane and the $(10\bar{1})$ plane. The equivalent effect along the (011) and (101) planes is not present and there is some indication that sputtering is blocked in planes parallel with the $(01\bar{1})$ and $(10\bar{1})$ planes but not passing through the centre.

With a sample temperature of 300° the spot pattern changes. Although all of the higher-temperature features are present the $(\bar{1}11)$ spot has a different appearance. It resolves itself into a sharply defined distorted hexagon which is hollow inside except for a darker diffuse area near the centre.

The breadth of the hexagon is found to be temperature dependent, as shown in Fig. 2. Extrapolation leads to a value of approximately 23° for the angle subtended by the hexagon at the sample when the temperature is T_a.

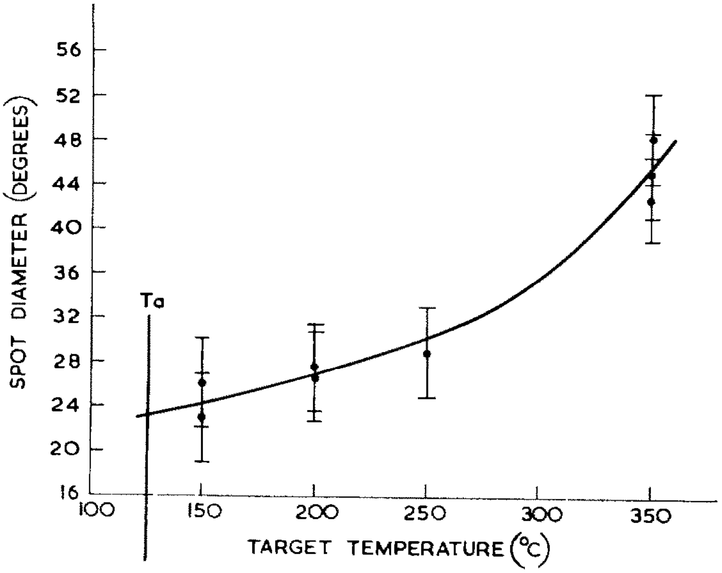

FIG. 2.—Variation of angular diameter subtended at the sample by $[\bar{1}\bar{1}\bar{1}]$ "spot" with sample temperature.

GaAs (111) *and* $(\bar{1}\bar{1}\bar{1})$. The effect of the surface layer on the sputtering of GaAs is shown clearly by the deposits from (111) and $(\bar{1}\bar{1}\bar{1})$. In both cases the deposit has a threefold symmetry but only the $(\bar{1}11)$ spots are clearly distinguishable. The $(\bar{1}11)$ spots appear as three almost circular hollow deposits from the (111) face and a single normal triangular deposit from the $(\bar{1}\bar{1}\bar{1})$ face. The (111) spots are either absent or so weak as to be lost in the background, as are the (100) spots which had been observed with a (110) surface.

GaAs (100). The appearance of spot patterns from GaAs (100) at temperatures above T_a is in accord with the patterns from (111) and (110). Spots due to $(\bar{1}11)$ are prominent as are (111) spots in this case. A blocking along planes between the spots is also noticeable, so (110) spots are absent.

Sputtering yields

The effect of temperature on the sputtering yield of GaAs (111) is shown in Fig. 3. The yield is invariant with temperature over a wide range above and below a region near T_a. The dependence of sputtering yield on ion energy for different surfaces over a range 8–16 keV was measured at fixed temperatures above and below T_a. Figures 4 and 5 show the results for GaAs (110), GaAs (100) and GaAs (111) at a sample temperature of 250°. The sputtering yields for all surfaces indicate that a maximum must occur in the yield/energy curves at below 8 keV.

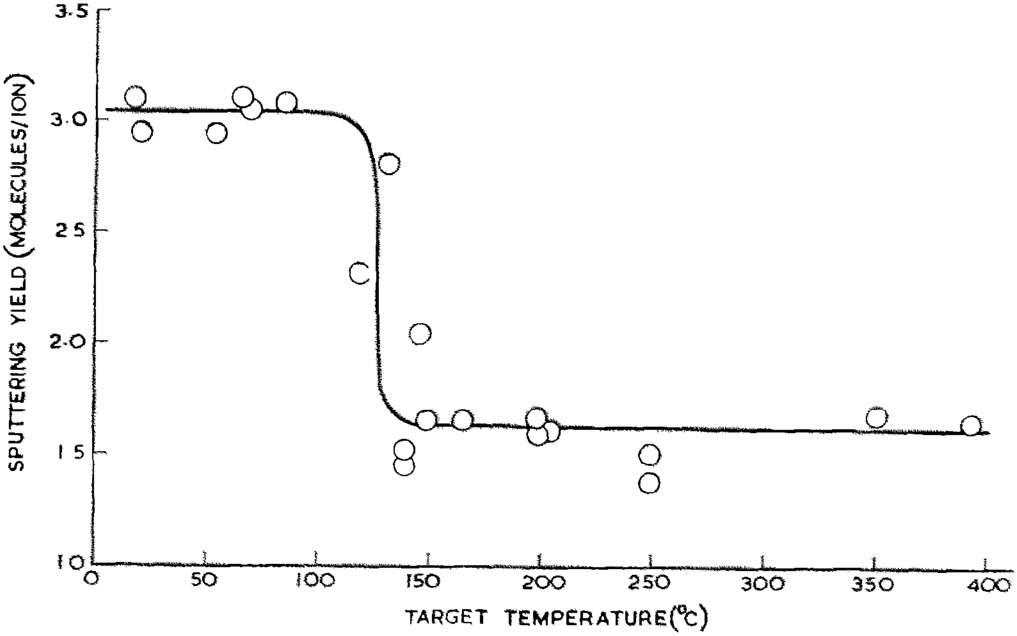

FIG. 3.—Graph of sputtering yield against target temperature for GaAs [111], 16 keV Ar$^+$.

Below T_a, the sputtering increases with ion energy as shown in Fig. 5. Under these conditions the sputtering yield is independent of the crystal surface. These results are compatible with the formation of an amorphous surface produced by radiation damage. Over the energy range studied, the low-temperature yields are higher than any of the high-temperature yields. It was found difficult to obtain reproducible results for low-temperature yields, whereas the high temperature measurements produced good results after the sample-handling procedure had been standardized. It is not clear why this occurred but small variations in the rate of formation of the amorphous layer might affect the overall yield.

Effect of bombardment on the surface

Microscopic examination of the surfaces after sputtering showed that the finely finished and flawless parts of the surfaces were sputtered off evenly both at high and low temperature but small flaws such as fine scratches or etch pits produced during preparation of the sample were rapidly expanded by erosion at temperatures below T_a, although they were not preferentially eroded at higher temperatures. We were unable to detect any difference such as has been described by Comas and Cooper,[9]

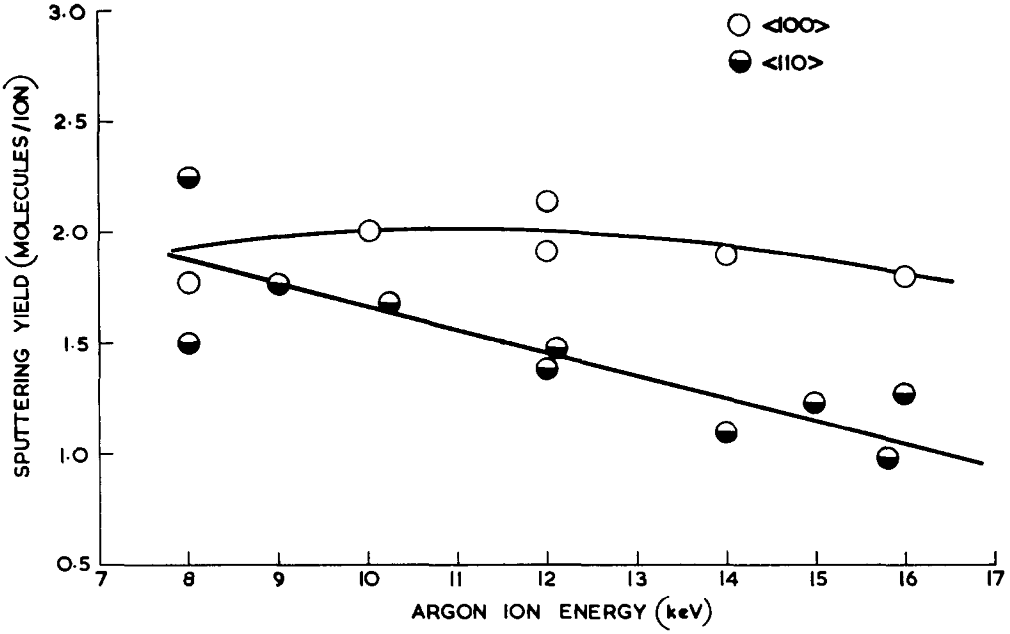

FIG. 4.—Sputtering yield *vs.* ion energy for a sample temperature of 250° for GaAs (100) and (110).

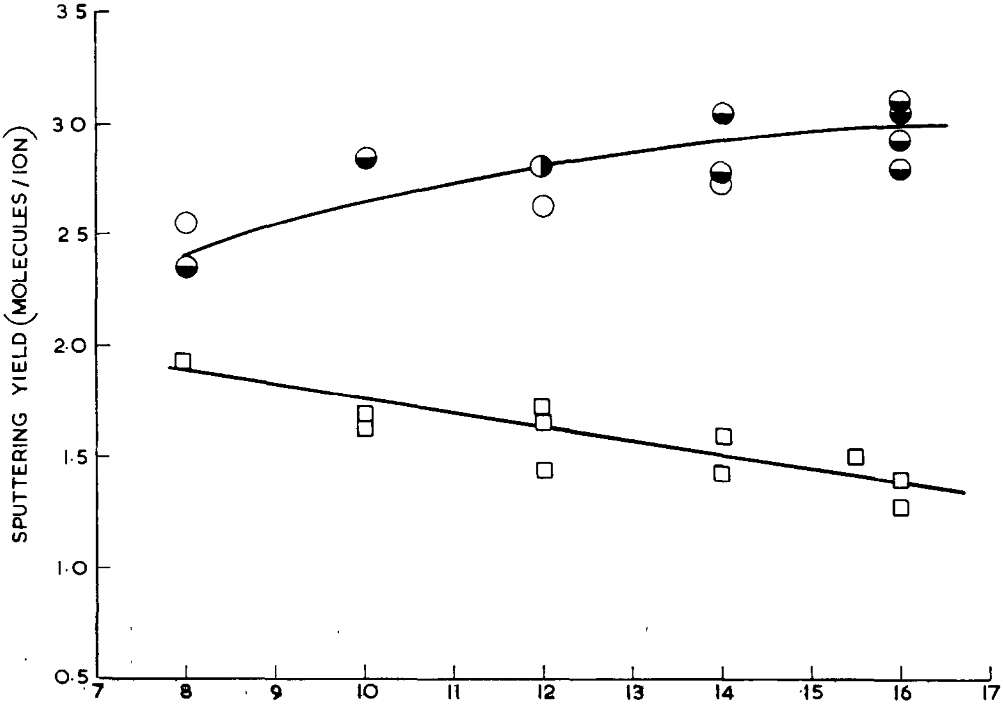

FIG. 5.—Sputtering yield against ion energy for a sample temperature of 20–70° (100), (110), (111) and 250° (111).

in the appearance of finely finished bombarded surfaces, irrespective of their orientation or temperature.

Composition of the sputtered deposit

The composition of the sputtered material was determined after depositing it on silica discs. These were cut to select various features of the sputtered pattern and subjected to neutron-activation analysis. Table I shows the gallium/arsenic ratio for the areas selected.

TABLE I.—THE AMOUNTS OF GALLIUM AND ARSENIC IN VARIOUS "SPOTS" FROM GaAs (111), (110), (100) AND PURE GaAs

Sample	"Spot" analysed	Ga, %	As, %	Error
[100]	$(\bar{1}\bar{1}\bar{1})$	57	43	±3%
[100]	(100)	49	51	
[100]	(111)	42	58	
[110]	$(\bar{1}\bar{1}\bar{1})$	55	45	
[110]	(111)	40	60	
[111]	$(\bar{1}\bar{1}\bar{1})$	64	36	
[111]	(111)	47	53	
[100]	at 50°C	51	49	±2%
Crystal	—	50	50	

Discussion

The most noticeable feature of the results of bombarding GaAs crystals with Ar^+ at 8–16 keV is the similarity to results obtained on GaAs and other semiconductors below 2 keV. There exists in all cases a transition temperature above which defects in the crystal surface are annealed out faster than they are produced by bombardment; above and below this temperature the sputtering yield is almost independent of temperature; well defined spot patterns are formed at temperatures above T_a in directions which correspond approximately to specific axes in the crystal and the composition of the spots depends on which crystal axis they correspond to.

All of these features must be explained by phenomena which are essentially energy independent, at least up to 20 keV.

The existence of a transition temperature in III–V and other semiconductors has been observed over a wide range of energies varying from a few hundred volts with Ge,[5] Si,[2] GaAs,[1] and InSb,[4] to 30 keV for Ge and Si.[10] A quantitative explanation of the phenomenon has been proposed by Anderson and Wehner[5] for energies up to 1 keV, based on the equilibrium between defects annealed out by thermal vibrations and defects produced by ion bombardment. Unfortunately, it is difficult to make a quantitative comparison over a wide range of energies because of the general paucity of results for any one semiconductor. The value of 125° obtained in this work at 16 keV and 4 $\mu A/mm^2$ can be compared with about 130° obtained by Anderson and Wehner at lower energies but higher current densities.

The temperature independent regions above and below T_a are of particular interest in the theory of sputtering. Whereas the penetration of ions through channels in single crystals is very temperature dependent (see for example the work of Channing and Howe[11,12]) the sputtering yields are very insensitive to temperature change over a wide range. Carlston *et al.*[13] have demonstrated this with 2–10 keV Ar^+ on several single crystal and polycrystalline metal targets, and Nelson[14] has shown that up to a temperature where thermal spikes are important the sputtering yield of many polycrystalline materials is temperature independent for 45 keV Xe^+, Ar^+ and Ne^+. Lehmann and Sigmund[15] have incorporated these and other results into a mechanism of sputtering which shows that spot patterns can be formed by as few as 2 or 3 regular lattice layers near the surface. The appearance of spot patterns from zinc blende structures is good evidence for long-range focussing contributing only a minor part to the sputtering mechanism.

Only two directions produce well defined spots in GaAs, the (111) and (100). The (111) spots are produced by all the surfaces examined and have appearances which depend on the polarity of the axis. By using the etching method of White and Roth[20] it was found that the $(\bar{1}\bar{1}\bar{1})$ directions, which produce the hollow spots, are on normals to the surface which have arsenic atoms as the outermost layer. That is, the atom which has the highest concentration in the centre of the sputtered deposit is the one which forms the second atomic layer below a stable (111) surface. As can be seen from the schematic Fig. 6, this atomic layer is bonded directly by a single bond to the third layer atoms. A nearest neighbour collision along this axis could be followed by assisted focussing at the surface layer. The centre spot found in the deposit from $(\bar{1}\bar{1}\bar{1})$ is compatible with an assisting lens of three atoms. The comparable concentration of both atomic components must indicate that, after the second layer atom is lost, rearrangement of the surface takes place and the remaining surface layer is more randomly ejected.

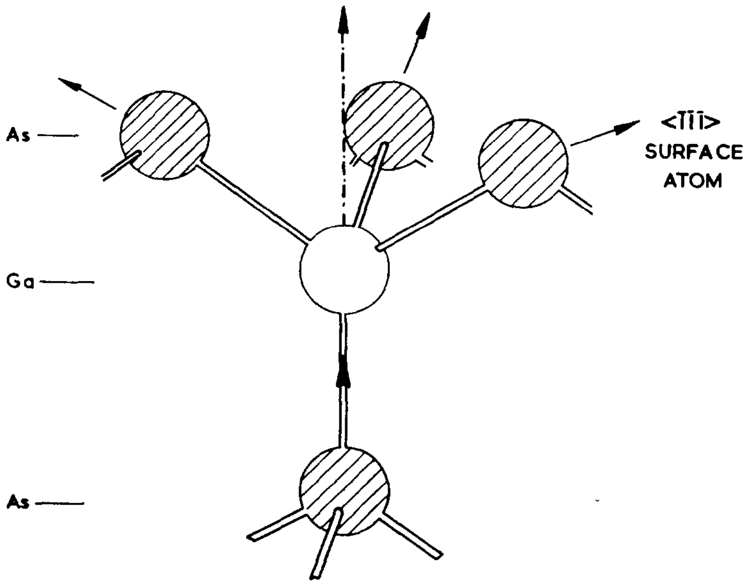

FIG. 6.—Schematic diagram of the $(\bar{1}\bar{1}\bar{1})$ surface atom arrangement.

The absence of polarity in the (100) direction is in agreement with (*a*) the similar form of the (100) and (010) spots from a [100] surface and (*b*) the composition of the spots being almost 50% Ga:50% As. The (100) spots are generally much weaker than those in the (111) directions as would be expected from directions in which the nearest neighbour pairs are absent. We find the centre spot for the [100] surface to be absent. It is difficult to understand how momentum transfer can occur at all in the (100) direction, because of the large separations between atoms along this axis, although we shall show later that at lower temperature (60–70°) there is some indication that interstitial argon atoms influence the sputtering of InSb.

The disparity between the theoretical and measured angles between certain spots has been noticed in Ge.[3] We find this to occur in GaAs, for which from the [100] and [111] surfaces the (111) spot directions are 49° ± 3° and 56° ± 3° respectively, compared with theoretical values of 54°44′ and 70°32′. Haneman[16] has proposed a model for the [111] surface of III–V semiconductors based on distortion of the bonds in the outermost layers by hybridization of the s and p orbitals on the surface atoms. This model is used to explain the decrease in azimuth angle of the spots from the theoretical. Haneman suggests that distortion of the surface atom bonds leads to a close-packed atom chain near the surface which facilitates the ejection of the surface atom at 55° to the surface normal. This value is close to the 59° quoted by Anderson and Wehner and to our value of 56°. Unfortunately, this model would imply that the spots would have a composition with a greater than stoichiometric amount of the surface layer atom. Based on the work of Roth and White our results show that the second layer atoms have the higher concentration for a given normal spot.

The hollow appearance of the $(\bar{1}11)$ spot is always present between T_a and about 300° irrespective of the surface being bombarded. The edge of the spot is very sharp in all cases and gives the impression that some form of blocking has occurred along the $(\bar{1}11)$ axis. We were not able to show by analysis if the edges of the spot were of a different composition from the centre but the surface texture leads us to believe that the material leading away from the edge was similar to the (111) or (100) spot material. That is, it was either stoichiometrically GaAs or had a slight excess of As. The large diameter of the spot can only be produced by blocking if the source of the sputtering is within one or two atom layers of the surface. Yurasova[7] and Anderson and Wehner[5] observed a similar spot formation in InSb. Yurasova proposed that momentum transfer along high index directions produced spots with hexagonal symmetry. However, the appearance and variation of diameter with temperature preclude this argument in our case. The low intensity of the (111) spot suggests that chemical bonding must play an important role in the sputtering of semiconductors; the atomic weights of Ga and As are so nearly the same that major differences due to momentum transfer can be excluded.

Comas and Cooper[9] have analysed mass-spectrometrically the neutral species sputtered from GaAs by 100 eV argon ions. They found that for a target at temperatures below T_a atomic Ga and As were the major products with a small amount of molecular GaAs, thus contradicting the opinion of Wolsky *et al.*[17] that molecules were the predominant species sputtered from GaSb. Surprisingly, Comas and Cooper found that the sputtering yield varied with the crystal surface although their conditions were such as to lead to an amorphous layer very quickly during bombardment.

The major difference between low-energy and high-energy bombardment is in the relative sputtering yield for different surfaces at different temperatures. Whereas Anderson[1] has found that for Ge the relative sputtering yields are in the order (100) > (111) at room temperature >(110) for GaAs bombarded by Ar^+ at greater than 10 keV we find that at room temperature the sputtering yield is higher than any crystal surface yield at temperatures above T_a, the order of these being (100) > (111) > (110). We interpret this as showing the importance of transparency at high energies. For a diamond lattice the relative opacities for (100), (111) and (110) directions are 0·23:0·20:0·16 in agreement with the range studies of high-energy Xe in Si.[18] If the atoms are randomized by ion bombardment the transparency will be lowered for all surfaces and the yields will accordingly be higher for room temperature measurements. It is generally true that an amorphous or polycrystalline target has a higher sputtering yield than a regular lattice and that the maximum in the yield/energy curve is at a higher energy; for equivalent penetration the effective collision cross-section must be lower for a random lattice than for a regular one.

The concept of transparency need not be totally rejected for the low energy region. As the penetration of incoming ions is very low for low-energy bombardment it can be shown that to a depth of about 1 cell unit the transparency of a surface containing randomly positioned atoms can be higher than for a (100) face and comparable to a (111) face, where atoms are held in fixed unfavourable positions with respect to the incoming beam. Nevertheless, it must be concluded that at low energies other factors than transparency (*e.g.*, binding energy) are important and this importance decreases as the energy increases. A crossover in the yield curves, which we observe in the region of 8 keV, has been reported by Wolsky and Zdanuk for argon on copper.[19]

CONCLUSION

The observations made here are in general agreement with other sputtering measurements made at low energies on semiconductors and at high energies on metal single crystals. However, certain unusual features are apparent and further investigation into the sputtering of regular two-component lattices may lead to an insight into the importance of properties such as binding energy in the sputtering process.

An analysis of the material sputtered from GaAs (111) surfaces indicates that a short-range assisted focussing of second layer atoms takes place at the surface as they are ejected.

Acknowledgement—We should like to thank Mr. D. Mapper for the neutron-activation analysis of our sputtered deposits.

Zusammenfassung—Ein Gerät zur Messung der Zerstäubungsausbeuten (*S*) von mit Argonionen beschossenen GaAs-Einkristallen wird beschrieben. Die Abhängigkeit von *S* von der Temperatur des Targets und der Ionenenergie sowie die Anisotropie der Zerstäubung bei hoher Temperatur wird diskutiert.

Résumé—On décrit un appareil pour la mesure des rendements en "crépitement" (*S*) de cristaux uniques de GaAs bombardés par des ions argon. On discute de la dépendance de *S* par rapport à la température de la cible et l'énergie des ions et de la nature anisotropique du crépitement à température élevée.

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MASS SPECTRA OF SOME BIVALENT TRANSITION-METAL ION CHELATES WITH PYRIDYLAZO PHENOLS AND NAPHTHOLS

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Summary—The mass spectra of 2- and 4-(2-pyridylazo)phenol, 2-(2-pyridylazo)-1- and 1-(2-pyridylazo)-2-naphthol and several chelates of these compounds with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) are discussed. Comparisons are made with the results of solution studies of complex formation of the same chelates.

PYRIDYLAZO PHENOLS, NAPHTHOLS AND RESORCINOL are now well established analytical reagents,[1] but the stoichiometry of several of the chelates is uncertain.[2-4] Mass spectrometry is, in principle, a good method for the establishment of stoichiometry and is a relatively unexplored approach.[5] Accordingly, we have obtained and examined the mass spectra of several chelates formed from these reagents and attempted to assess the value of mass spectrometry in the study of chelate chemistry.

EXPERIMENTAL

Reagents

Pyridylazo derivatives. 2-(2-Pyridylazo)phenol(*o*-PAP), 4-(2-pyridylazo)phenol(*p*-PAP), 2-(2-pyridylazo)-1-naphthol(*o*-α-PAN) and 4-(2-pyridylazo)-1-naphthol(*p*-α-PAN) were synthesised by reacting 2-hydrazinopyridine[6] with 1,2-benzoquinone, 1,4-benzoquinone, 1,2-naphthoquinone or 1,4-naphthoquinone respectively.[7,8] The quinones were either obtained commercially and purified before use or synthesized by published procedures. *o*-α-PAN was also prepared by the method described earlier.[9] 1-(2-Pyridylazo)-2-naphthol(*o*-β-PAN) was obtained commercially. All the reagents were purified by recrystallization from 50% aqueous methanol or by sublimation. All were subjected to elemental analysis for carbon, hydrogen and nitrogen; the results were in agreement with the theoretical within the usual limits of accuracy. The mass spectra described below confirmed the purity of all but *o*-α-PAN, which contained approximately 1% impurity with a molecular weight 28 amu greater than *o*-α-PAN. This impurity was found in samples prepared by different methods and in the chelates of *o*-α-PAN. It is possibly a tetrazo derivative, but further work is needed to verify this.

p-α-PAN could not be purified by these methods (it exploded rather than sublimed and gave tars on recrystallization) and consequently was not examined further.

Metal ion solutions. Solutions were prepared from analytical reagent grade salts and standardized by titration with EDTA.

Chelates. Equal volumes of equimolar ($5\cdot0 \times 10^{-3}M$) solutions of metal ion in water and PAP or PAN in ethanol were mixed and a few drops of aqueous ammonia were added to ensure complete reaction. The solutions were heated and then allowed to stand whilst the chelate precipitated. This was then washed with water and dried *in vacuo*. This procedure generally yielded crystalline products.

Apparatus

Mass spectrometer. Spectra were obtained on solid samples with an A.E.I. MS9 double focussing mass spectrometer. One spectrum was run at a resolution of 15000 with heptacosafluorotributylamine as a reference; the rest were run at low resolution.

RESULTS AND DISCUSSION

Mass spectra of ligands

The spectrum of each ligand shows a well-defined parent peak and a similar fragmentation pattern (Figs. 1–4).

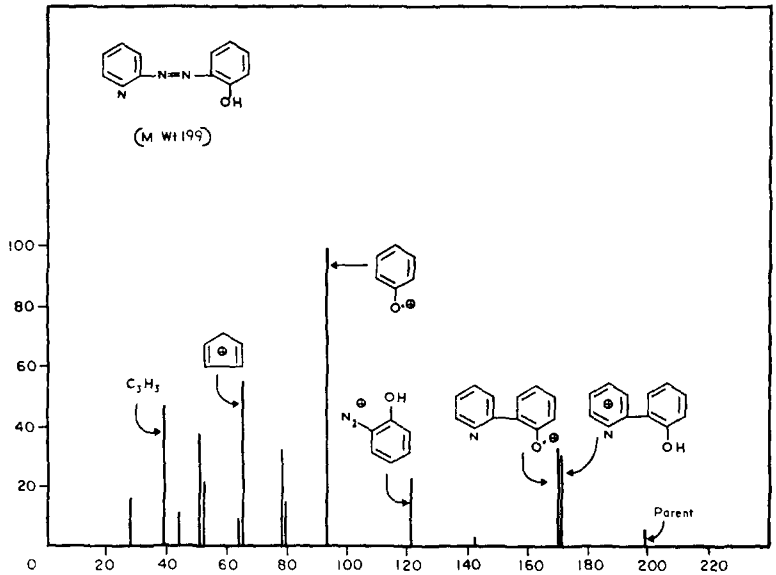


FIG. 1.—Mass histogram of 1-(2-pyridylazo)phenol (*o*-PAP). Temp. 200°C.

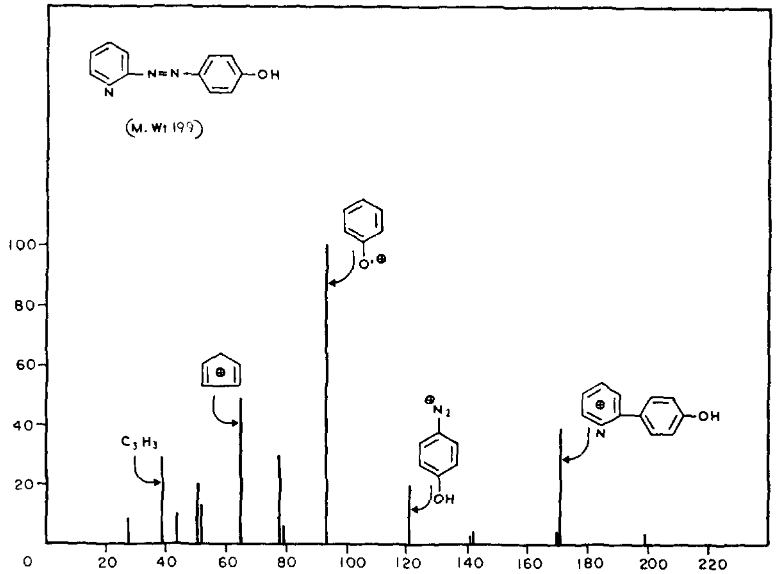


FIG. 2.—Mass histogram of 4-(2-pyridylazo)phenol (*p*-PAP). Temp. 250°C.

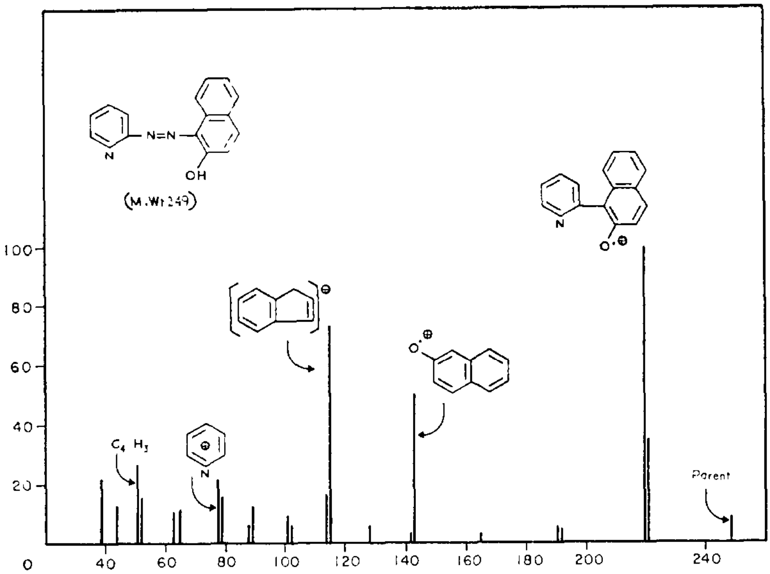


FIG. 3.—Mass histogram of 1-(2-pyridylazo-)-2-naphthol (*o*-β-PAN). Temp. 250°C.

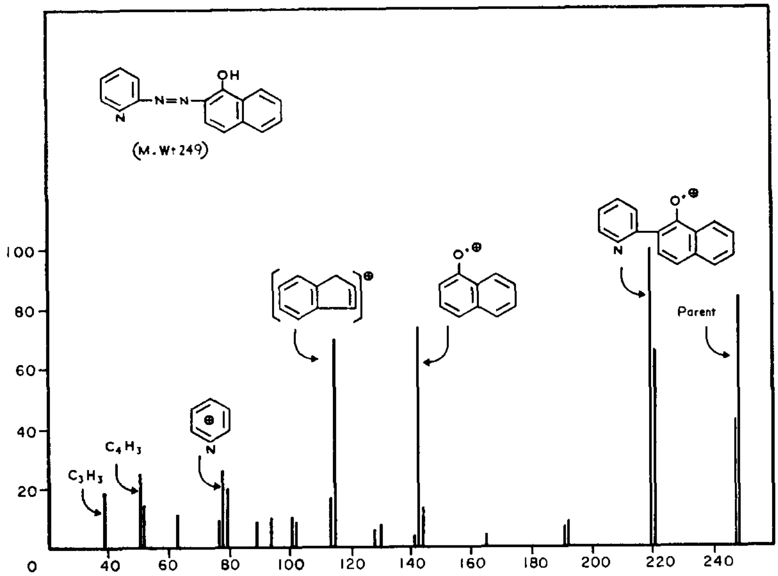


FIG. 4.—Mass histogram of 2-(2-pyridylazo)-1-naphthol (*o*-α-PAN). Temp. 270°C.

1-(2-*Pyridylazo*)*phenol*, (o-*PAP*). The spectrum of this ligand is typical and is discussed in detail to show the general pattern of fragmentation. The pathways of breakdown are summarized in Fig. 5. Steps accompanied by metastable peaks are known with certainty,[10,11] because they proceed according to the well-known relationship between parent, m_1, daughter, m_2, and metastable, m^*, *i.e.*, $m^* = m_2^2/m_1$. Other postulated steps are those that best fit the facts for reasons given below.

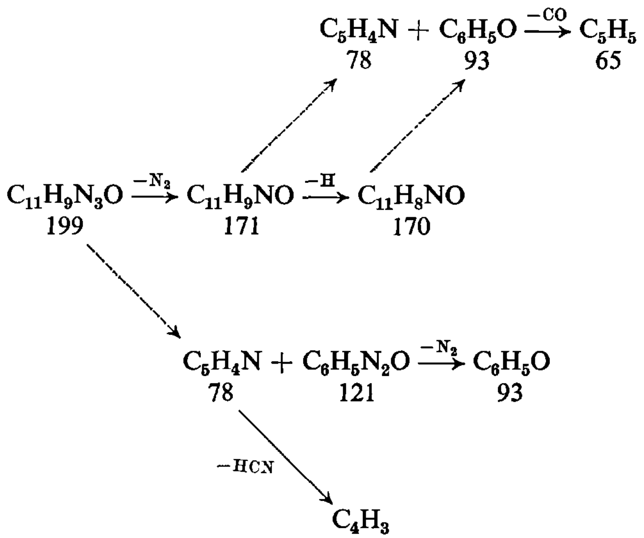
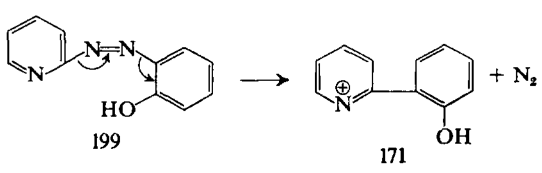


Fig. 5.—Fragmentation pattern of 1-(2-pyridylazo)phenol.
Solid lines—steps accompanied by metastable peak.
Dotted lines—steps unaccompanied by metastable peak.
Numbers indicate value of *m*/*e*.

There is a peak at *m*/*e* 199† due to the parent ion, which then fragments in two ways: (*i*) by loss of nitrogen and (*ii*) by cleavage resulting in pyridine and phenolazo fragments.

(*i*) The loss of nitrogen is confirmed by a metastable peak at 171. It is probable that the mechanism is that indicated by



The recombination of the pyridine and phenol fragments with retention of the substitution patterns of the pyridine and phenol is suggested by the difference in fragmentation pattern of *o*- and *p*-isomers. The fragment corresponding to *m*/*e* 171 then breaks down by one of two routes, (*ia*) or (*ib*).

(*ia*) Loss of a hydrogen atom gives 170 (shown by a metastable peak at 169 on loss of another). The ratio of the abundance of 171 and 170 in the ligand and chelate

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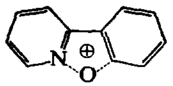
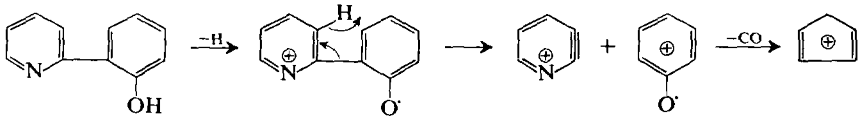
† For convenience of discussion, units of *m*/*e* may be assumed and all fragments are named as if they did not carry any charge.

spectra show that it is the phenolic hydrogen that is lost. Comparison with *p*-PAP indicates that proximity of oxygen and nitrogen atoms may result in intermediates which facilitate the reaction, *e.g.*,



The next step is probably transfer of a proton from the pyridine to the phenolic ring with consequent cleavage of the bond between the rings. A metastable peak at 45·4 confirms the loss of carbon monoxide from the phenolic fragment 93 to give a five-membered ring. The steps of (*ia*) are



171 170 93 65

The minor peak at 142 may be due to the loss of carbon monoxide from 170.

(*ib*) There is an immediate rupture of the bond joining the rings without prior loss of hydrogen. The great abundance of 93 and 78 shows this to be a major pathway. Pyridine loses hydrogen cyanide to give C_4H_3.

(*ii*) The peak at 121 is probably due to a phenolazo fragment formed by cleavage of the azo-nitrogen pyridine bond of the parent. There is a loss of nitrogen (metastable 71·5) to give a peak at 93.

4-(2-*Pyridylazo*)*phenol*, (p-*PAP*). The spectrum is very similar to that of *o*-PAP and the fragmentation pattern can be interpreted in the same way. The only major difference is the ratio of peaks 171 and 170 commented upon above. An accurate mass measurement of peak 171 gave 171·0684. This confirms the formula $C_{11}H_9NO$ and the elimination of nitrogen postulated above.

1-(2-*Pyridylazo*)-2-*naphthol*(o-*β*-*PAN*). The spectrum and mechanism of fragmentation are very similar to those of *o*-PAP, with naphthol being substituted for phenol. The postulated mechanism is shown in Fig. 6, which is self-explanatory. The differences noted are that the direct cleavage step (*ii*) is not noticeable and the ratio of peaks 221 : 220 compared with 171 : 170 of *o*-PAP is different and in favour of hydrogen loss.

$$\begin{tikzcd}
 & & & C_4H_3 & & C_9H_7 \\
\underset{249}{C_{15}H_{11}N_3O} \arrow[r, "-N_2"] & \underset{221}{C_{15}H_{11}NO} \arrow[r] \arrow[dr, "-H"] & \underset{78}{C_5H_4N} \arrow[ur, "-HCN"] & + & \underset{143}{C_{10}H_7O} \arrow[ur, "-CO"'] & \\
 & & \underset{220}{C_{15}H_{10}NO} \arrow[urr, "-C_5H_3N"'] & & &
\end{tikzcd}$$

FIG. 6.—Fragmentation pattern of 1-2(pyridylazo)-2-naphthol.

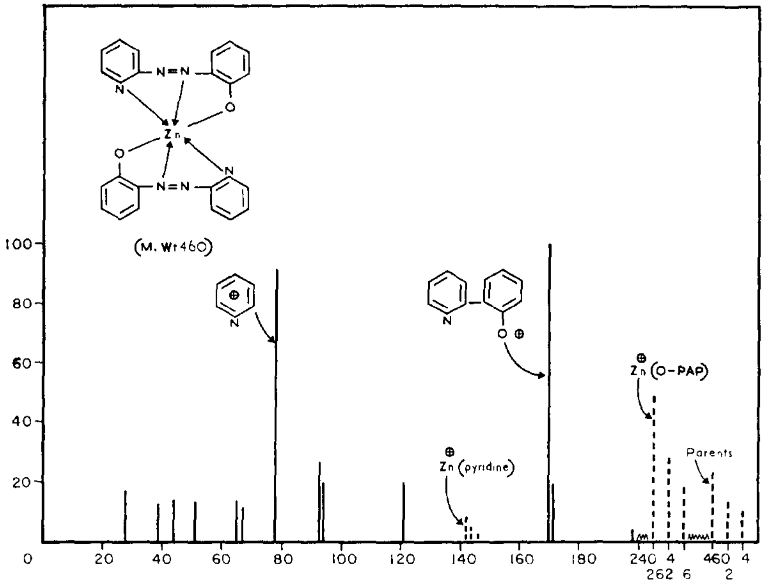


FIG. 7.—Mass histogram of chelate of zinc(II) and *o*-PAP. Temp. 400°C. ⁓⁓ = scale shortening.

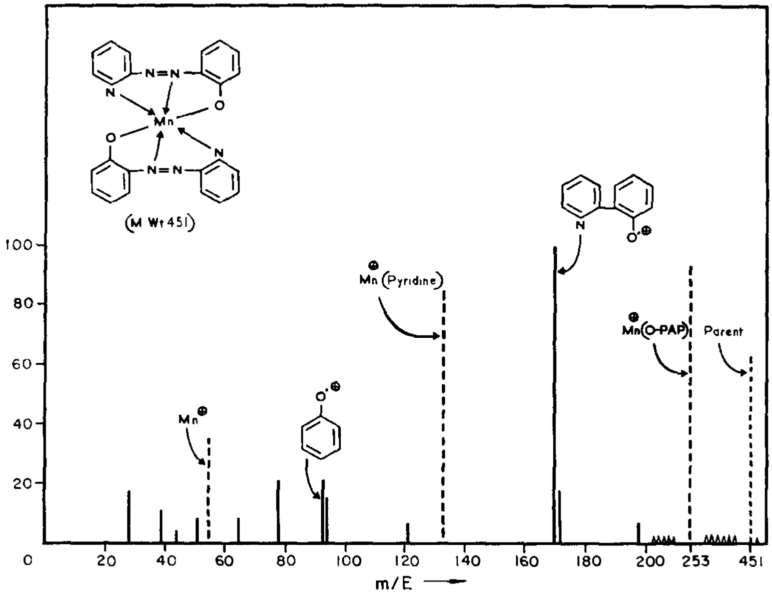


FIG. 8.—Mass histogram of chelate of manganese(II) and *o*-PAP. Temp. 380°C. ⁓⁓ = scale shortening.

2-(Pyridylazo)-2-naphthol, (*o*-α-*PAN*). The spectrum (Fig. 4) is virtually identical with that of *o*-β-PAN, except for a large peak at 248 due to the parent minus hydrogen. The breakdown of this ion appears to follow a route analogous to (*ii*) of *o*-PAP.

Mass spectra of chelates

The spectra of the chelates examined (Figs. 7–13), with the exceptions of *p*-PAP compounds, are all similar. A parent peak is observed, but the peak due to the parent minus one ligand is stronger and very useful diagnostically.

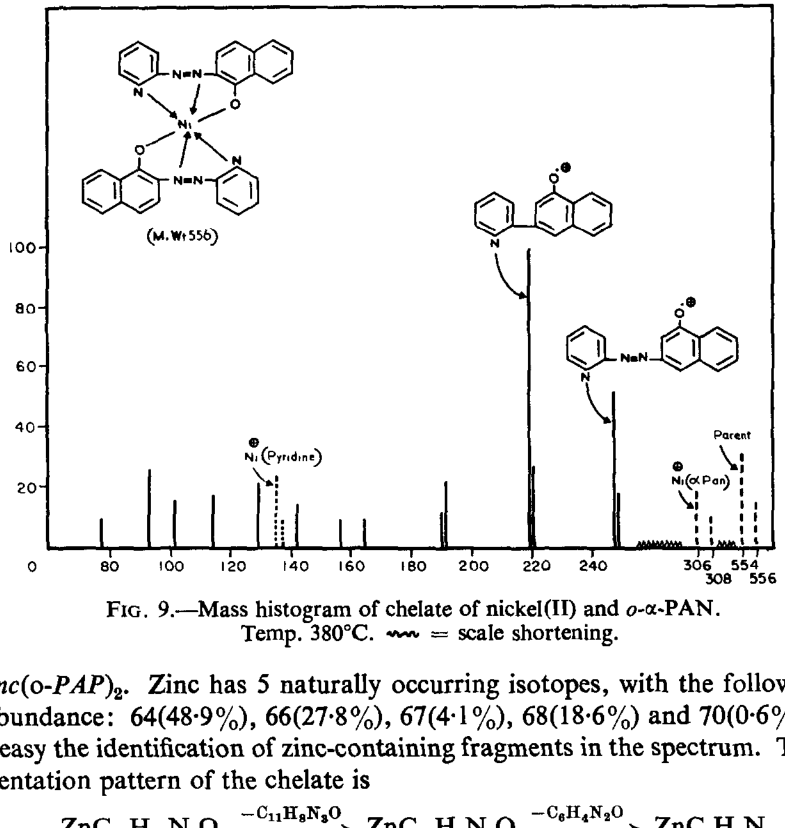


FIG. 9.—Mass histogram of chelate of nickel(II) and *o*-α-PAN. Temp. 380°C. ⁓ = scale shortening.

Zinc(o-*PAP*)$_2$. Zinc has 5 naturally occurring isotopes, with the following mass and abundance: 64(48·9%), 66(27·8%), 67(4·1%), 68(18·6%) and 70(0·6%). These make easy the identification of zinc-containing fragments in the spectrum. The major fragmentation pattern of the chelate is

$$\begin{array}{ccccc} ZnC_{22}H_{16}N_6O_2 & \xrightarrow{-C_{11}H_8N_3O} & ZnC_{11}H_8N_3O & \xrightarrow{-C_6H_4N_2O} & ZnC_5H_4N \\ 464,462,460 & & 266,264,262 & & 146,144,142 \end{array}$$

with loss of one ligand followed by cleavage to give monopryidinezincate (146,144,142) and azophenolate (121). The ligand fragments follow the fragmentation pattern of the parent ligand. The large peak at 170 due to the ligand minus nitrogen and hydrogen, and the absence of a metastable peak at 169, show that a proton is lost during chelation; the parent peaks at 464, 462 and 460 demonstrate a stoichiometry of 1:2 metal:ligand. The spectra thus confirm the results of solution studies.

There are also minor peaks containing zinc at P — 28 and P — 121, where P is the parent peak *m*/*e*, corresponding to loss of nitrogen and azophenolate respectively.

Nickel(o-*PAP*)$_2$. The doublet due to the most abundant isotopes of nickel, mass 58 and 60 and abundance 67·9% and 26·2%, enable nickel-containing fragments

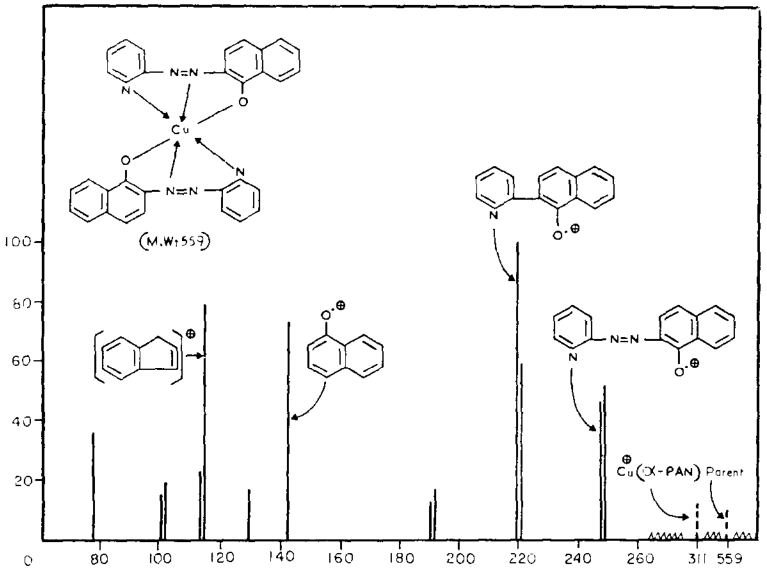


Fig. 10.—Mass histogram of chelate of copper(II) and *o*-α-PAN. Temp. 370°C. ﹏ = scale shortening.

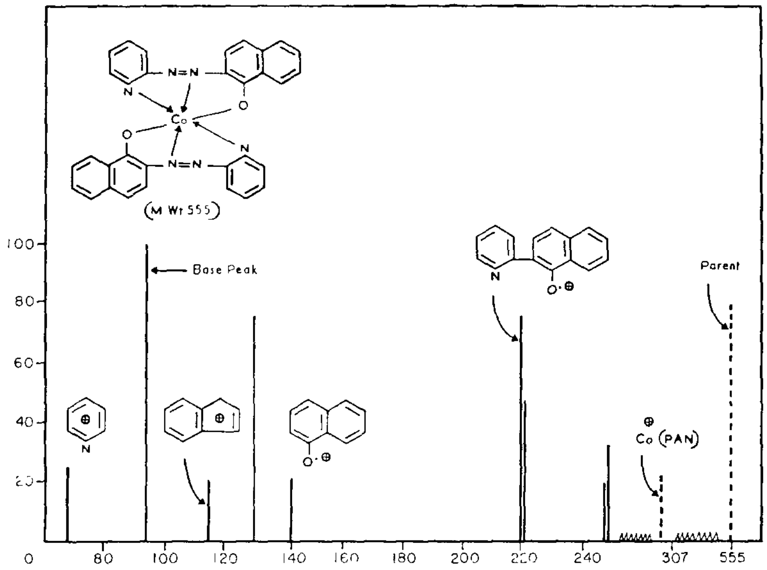


Fig. 11.—Mass histogram of chelate of cobalt(II) and *o*-α-PAN. Temp. 380°C. ﹏ = scale shortening.

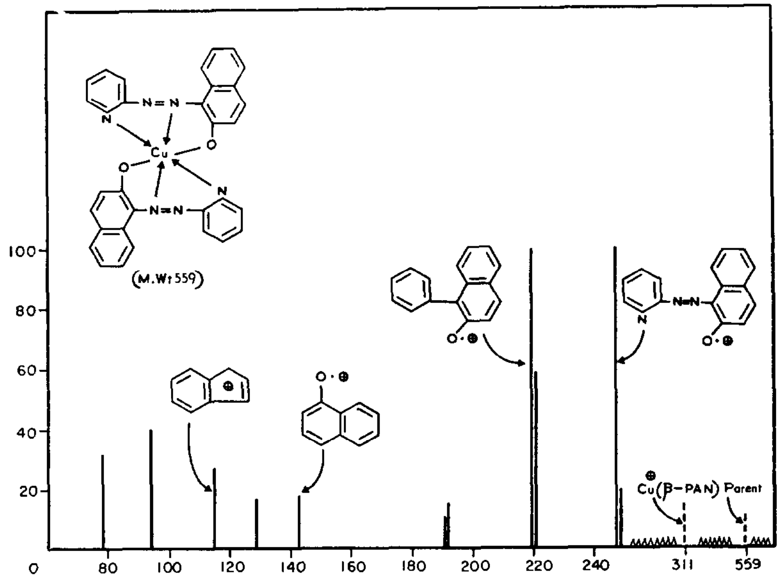


Fig. 12.—Mass histogram of chelate of copper(II) and *o*-β-PAN. Temp. 380°C. ﹏ = scale shortening.

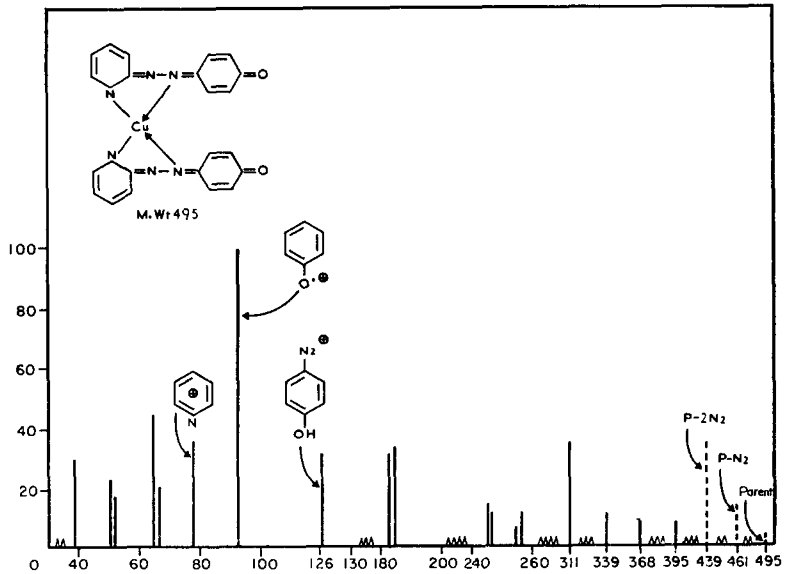


Fig. 13.—Mass histogram of chelate of copper(II) and *p*-PAP. Temp. 360°C. ﹏ = scale shortening.

to be readily identified. The spectrum is identical with that for Zn(*o*-PAP)$_2$ when the difference in atomic weight is taken into account.

Manganese (o-*PAP*)$_2$. There is only one stable isotope of manganese, but when allowance is made for this and the difference in atomic weight the spectrum (Fig. 8) is almost identical with that of Zn(*o*-PAP)$_2$. The major difference is the appearance of a peak at 55, which if due to manganese-55 implies a change of oxidation state from II to I.

Chelates formed between o-α-*PAN and zinc*(*II*), *nickel*(*II*), *manganese*(*II*)

The spectra and fragmentation pattern of these chelates is completely analogous to that of the corresponding *o*-PAP chelate; that of Ni(*o*-α-PAN)$_2$ is shown (Fig. 9);

Copper (o-α-*PAN*)$_2$. Copper has 2 stable isotopes of comparable abundance. 63 (69·1%) and 65 (30·9%). The most unusual feature of the spectrum is that there is no evidence of the expected doublet at M and M + 2, where M is the value of *m*/*e* for any ion containing copper-63 (Fig. 10). In all other respects the spectrum is in accord with that expected for copper-63. The possibility of the spectrum being a memory can be discounted because the spectrum shows the presence of *o*-α-PAN and peaks at *m*/*e* >249 which are not found in the other *o*-α-PAN chelate spectra. The possibility of *o*-α-PAN chelating with copper-63 preferentially is not in accord with general chemical experience or the results of solution studies on the system. Further, the spectrum we have obtained of copper acetylacetonate shows the expected isotopic pattern. This curious behaviour is being investigated in more detail.

Cobalt (o-α-*PAN*)$_2$. We have not yet examined the solution chemistry of the reaction between cobalt(II) and *o*-α-PAN, but the complex formed with *o*-β-PAN is unstable in air. The spectrum of Co(*o*-α-PAN)$_2$ (Fig. 11) shows signs of decomposition not observed in the other spectra of *o*-α-PAN chelates. There are several peaks unaccounted for and a large peak at 44 due to carbon dioxide. However, there is a parent ion peak at 555 confirming the 1:2 stoichiometry of the chelate, and a peak at 307 corresponding to the 1:1 chelate fragment, which suggests that the general fragmentation pattern is the same.

Chelates formed between o-β-*PAN and zinc*(*II*), *manganese*(*II*) *and copper*(*II*)

The spectra were very similar to those of the corresponding *o*-PAP and *o*-α-PAN chelates; Fig. 12 is representative. One difference is that the parent peak is much smaller than it is in the spectra of *o*-PAP and *o*-α-PAN chelates, where it is always a major peak and in one instance, is the base peak. The expected isotopic distribution is not found in the spectrum of the copper chelate, which behaves as though copper-63 were the only stable isotope of copper.

Chelates between p-*PAP and copper*(*II*), *nickel*(*II*), *cobalt*(*II*) *and iron*(*II*)

p-PAP forms chelates with fewer metals than *o*-PAP and those that are formed have different solubilities. For example, the manganese chelate is not formed. These differences are explained by the facts that *p*-PAP is bidentate and that the ionizable proton is not at the centre of chelation. Thus, in the neutral chelate the ligand is probably in the quinonoid form and has adducts such as ammonia or water if the metal ion is in an octahedral configuration. Support for these deductions is found in the spectra, which are quite different from those discussed above.

The compounds are much less volatile and the spectra were obtained at the maximum temperature of the probe. Under these conditions the chelate falls apart and the major peaks in the spectrum are those observed for the free ligand ion. In the spectra of the copper, nickel and cobalt complexes there are several common minor peaks of great interest. The copper chelate (Fig. 13) is taken as typical; the figures are based on copper-63, again the only isotope appearing in the spectrum. The peak at 459, corresponding to Cu(p-PAP)$_2$, is observed, but in addition there are peaks at 439, 467 and 495. The latter could correspond to two water molecules or two ammonium ions. The spectra are not of sufficiently high resolution to decide unambiguously between these two. The peaks at 467 and 439 could correspond to the successive loss of nitrogen from 495, as in the minor pattern noted with *o*-PAP chelates. The spectra are too weak to show with certainty the metastable peaks accompanying these losses. The peaks between 495 and 198, the ligand ion, are common to all the spectra and therefore do not contain the metal ion. They must be peaks due to recombination of the ligand fragments of the type noted in the spectrum of bis[2-(4-toluenesulphonamido]anilinecopper(II). It is not at all clear what the peaks actually correspond to but the following suggestions are in accordance with the observed mass differences: 311, loss of copper (63) and phenylazo (121) from parent; 339 and 246, loss of copper and one or two phenoxide (93) fragments from parent; 368, loss of copper and two water molecules from parent; recombination of the fragments remaining after these losses take place. Spectra of higher resolution are clearly required.

The spectrum of the cobalt complex does not show a parent ion peak at the expected value, but a peak at 246 suggests that it, like copper and nickel, has two co-ordinated water molecules.

The ion abundance, A, of the iron complex is given below. There are no peaks greater than that of the ligand ion, 198, but the fact that 199 is absent, *i.e.*, no protonated ligand, suggests that it conforms to the major fragmentation pattern of the other p-PAP chelates.

m/e	198	170	154	142	121	93	78	65	52	51	39	28
A, %	1·8	45·4	1·6	3·0	26·6	100	17·9	42·0	15·6	76·3	32·9	7·9

Comparison of results from mass spectra and solution studies

Ligands. It is difficult to prepare pure PANs and sometimes difficult to prove the identity of the isomer isolated. Because of the large molecular and equivalent weight, elemental analysis and titration to determine the equivalent weight can give uncertain results. Mass spectrometry is very useful in these circumstances, provided the compound is volatile and stable enough to give a reasonable spectrum. It is especially valuable as a method of quality control during purification steps. There are small differences between the spectra of *o*- and *p*- compounds and these were sufficient to confirm that *o*-α-PAN was incorrectly identified, as *p*-α-PAN, when first examined as an analytical reagent.[9] Whether this evidence is preferable to that from infrared spectra is a matter of taste and experience; both methods give correct identification of the isomer, provided that there is a sufficient number of reliable reference compounds available, but neither explains the large difference in pK_{OH} between *o*-α-PAN and *o*-β-PAN, which was the cause of the original misidentification.

Chelates of o-*α-PAN and* o-*β-PAN.* In solution work it is generally found that

o-α-PAN forms complexes more rapidly and with no ambiguity about the stoichiometry. We feel that it is better than o-β-PAN, which is nevertheless a very good analytical reagent. The mass spectra of o-α-PAN chelates show a constant stoichiometry of 1:2, a large parent peak and no adducts such as ammonia or water. The spectra of o-β-PAN chelates are identical except for the smaller parent peak. From these results it is possible to deduce that the ligands are terdentate and that the complexes are stable, but that those of o-α-PAN are the more stable.

The 1:2 stoichiometry of the copper(II) complex of o-β-PAN is most interesting, especially as the ratio of the peak of the 1:1 complex to the parent peak is not noticeably greater than that found for the other o-β-PAN chelates. The relative importance of the 1:1 and 1:2 complex in solution has been controversial from the time of the second measurement of the stability constants. The best assessment of the published work[2] is that the 1:1 complex is much more stable than the 1:2 complex and that in the latter o-β-PAN is bidentate. The recent crystallographic study by Fernando[2] would seem to have confirmed this view, but the mass spectrum suggests that the 1:2 complex is stable and the ligand is probably terdentate. The single crystal for the X-ray study was grown from a weakly acid solution whereas the compound was precipitated from alkaline solution in this study, but further work is needed to establish whether this is an important difference. The mass spectrum is singularly useful in determining the stoichiometry in this instance, because several workers have found it difficult to obtain a satisfactory elemental analysis of this chelate. The instability of the cobalt complexes and the complexity of their spectra have been noted above.

Chelates of o- *and* p-*PAP*. The mass spectra of o-PAP chelates support the conclusions of solution studies[12–14] and are so clear that they could usefully have preceded a solution study. The same cannot be said of the rather confusing spectra of p-PAP chelates. However there are points of interest that derive from the spectra. First, the spectra indicate the likelihood of mixed complexes being formed; this has not been inferred from the solution studies made to date. Second, the absence of adducts in the o-PAP spectra suggests that the ligand is terdentate, a view supported by solution and X-ray studies. Third, a correct assignment of the rearrangement fragments in the spectra of p-PAP chelates would be very valuable in deducing the correct stereochemical arrangement of the isomer; this type of information is not available from solution work and promises to be an area where mass spectrometry can contribute most to the understanding of chelates.

Fragmentation patterns of mass spectra

In addition to the spectra discussed above, the mass spectra of chelates of acetylacetone,[15] benzoylacetone,[16] *N*,*N'*-ethylenebis-(benzoylpropylideneimine),[17] 8-hydroxyquinoline,[18] dimethylglyoxime[19] and 2-(4-toluenesulphonamido)aniline[20] have been recorded. Although it is already obvious that there are great differences in the fragmentation patterns of the different chelates, there are several points of similarity. Spectra which are clean and have a well-defined parent peak show evidence of fragmentation by loss of one ligand molecule as a first step. Spectra without a parent peak may exhibit rearrangement of ligand fragments,[21] which is useful in supplementing other studies but can be confusing initially (unless high resolution spectra can be obtained).

The stoichiometry suggested by the spectra must be interpreted with care, because the peaks due to fragments of lower stoichiometry may be so much more intense than the parent that the parent peak is not detected. Thus the operator of the spectrometer must ensure that the part of the spectrum corresponding to the parent peak is scrupulously examined. We have also obtained the spectra of several acetylacetonates, which are in good agreement with those already published. There is no evidence of the hydrates or polynuclear chelates known from X-ray and solution work to exist.[22] Although absence of a peak may not be conclusive, presence of one is, and this may be extremely valuable in resolving a difficult problem of stoichiometry.

Shannon and Swan[15] have argued that the number of electrons in a fragment is important for stability and that stability of chelate fragments may be obtained by change in oxidation state. We have only found good evidence of such changes in the chelates of manganese; none in the chelates of cobalt and copper, which would be expected to behave in a similar manner. However, we cannot be dogmatic about this because the spectrum has so many peaks at the lower end that we were unable to determine the final fate of the metal ion. The calculated energies of the bonds in amine complexes[23] suggest that in a chelate the metal ligand bond may be the weakest, so the two postulated routes—loss of one or both ligands—may be the most likely, regardless of electron balance. Certainly it is true that a much greater difference exists between spectra of complexes of the same metal with different ligands than between complexes of the same ligand with different metals.

We have noted that the spectra of the copper chelates do not show the expected isotopic distribution. This is an observation which we are unable to explain, but if the phenomenon is more widespread it could cause confusion in spectral interpretation.

Acetylacetonates and chelates of *o*-PANs and *o*-PAP sublime and this may be a significant factor in their spectra being well defined and containing a parent peak. However useful spectra may be obtained with unstable or involatile compounds.

CONCLUSION

Low resolution mass spectra of metal chelates of pyridylazophenols and naphthols can be easily obtained and are very valuable in interpreting or confirming the findings of other methods. There are limitations to the method and it is fundamentally a supplementary method. The 1:1 chelate fragments are very well defined and it may be possible to base analytical methods on them.

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Zusammenfassung—Die Massenspektren von 2- und 4-(2-Pyridylazo)-phenol, 2-(2-Pyridylazo)-1- und 1-(2-Pyridylazo)-2-naphthol und mehreren Chelaten dieser Verbindungen mit Mangan(II), Kobalt(II), Nickel(II), Kupfer(II) und Zink(II) werden diskutiert. Vergleiche werden angestellt mit den Ergebnissen von Untersuchungen der Bildung derselben Chelate in Lösung.

Résumé—On discute des spectres de masse des 2- et 4-(2-pyridylazo) phénol, 2-(2-pyridylazo)1- et 1-(2-pyridylazo)2-naphtol et de plusieurs chélates de ces composés avec: manganèse(II), cobalt(II), nickel(II), cuivre(II) et zinc(II). On effectue des comparaisons avec les résultats d'études en solution de formation de complexe des mêmes chélates.

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CHEMICAL ANALYSIS OF CERAMIC MATERIALS, CONTAINING URANIUM AND PLUTONIUM, ARISING FROM THE DEVELOPMENT OF NUCLEAR FUELS

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Summary—A comprehensive and critical review of analytical methods used in nuclear fuel technology.

THE oxides, carbides, nitrides, silicides and phosphides of plutonium and uranium possess in varying degree the properties of chemical integrity, high melting point, high density and high thermal conductivity, which are attractive to the nuclear fuel technologist. The evaluation of these materials from the scientific and economic point of view calls for considerable technical effort requiring analytical support at various stages. These stages and the analytical support required can be summarized as follows:-

1. Preparation of an individual compound on the gram scale. Analysis is required to define stoichiometry.
2. Preparation of mixtures of compounds with the addition of fission products and other elements for phase diagram studies. Analysis is necessary to determine the final composition, which might have changed from that intended during the course of preparation.
3. Preparation of potential nuclear fuels for irradiation testing. Analysis is required to control the composition within the limits specified and to check homogeneity.
4. Post-irradiation examination. An important requirement for any experimental fuel is a study of its behaviour under irradiation in a nuclear reactor. After the irradiation of test specimens, one of the main requirements from the analytical chemist is the determination of burn-up, or the degree of irradiation, undergone by these specimens.

Two major difficulties are common to all four stages defined above. First, the ceramic nature of the materials poses a difficult problem at the outset of any projected chemical analysis, and secondly the radioactivity, α in stages 1–3 and $\alpha\beta\gamma$ in stage 4, imposes handling and other restrictions during the analytical procedure. Both these difficulties influence the selection and development of methods of analysis, and detailed recommendations for each type of material are given. The ceramic materials mentioned above have not all been fully evaluated as nuclear fuels, and for this reason the section on post-irradiation examination is limited to the oxides and carbides of plutonium and uranium.

PRE-IRRADIATION ANALYSIS

The ceramic nature of the materials poses a difficult dissolution problem at the outset of any projected chemical method of analysis, and the radioactivity of the plutonium demands careful handling in glove boxes during the analysis.

Methods of dissolution

The method of dissolution used depends not only on the chemical nature of the ceramic but also on the element to be determined. Table I indicates the wide variety of materials with which experience has been gained in the Analytical Sciences Division at A.E.R.E.

Oxides. Plutonium dioxide, particularly after ignition at high temperatures ($>1000°$) is notoriously difficult to dissolve in mineral acids.[1-3] Fusion in ammonium bisulphate is the preferred method of dissolution before electrochemical methods[4] of determination, but the more rapid sodium peroxide sinter has been employed as a preliminary to the spectrophotometric determination of plutonium.[5] If the plutonium dioxide is in complete solid solution with uranium dioxide the material can be dissolved in hot $8M$ nitric acid[6] but this condition cannot be assumed in unknown samples.

Carbides. The acid dissolution of heavy element carbides is always accompanied by the liberation of graphite and a mixture of organic products.[7] These are undesirable, particularly if electrometric or spectrophotometric methods of analysis are to be employed. This difficulty can be minimized by carrying out the initial dissolution with hot $8M$ nitric acid, which prevents the deposition of graphite and solid organic products, followed by evaporation to fumes of sulphuric acid and wet oxidation of organic matter with nitric acid. The use of fuming perchloric acid, although highly effective for the destruction of unwanted organic material, is considered to be too dangerous to be employed routinely under the conditions normally prevailing in glove-box operations. There would, however, be no objection to the use of fuming perchloric acid in plutonium analytical chemistry in a suitable fume-cupboard, but under these conditions the quantity of plutonium used should not exceed 10 mg.

An alternative approach to the dissolution of a carbide material is to carry out a controlled oxidation in air at low temperature, and subsequently treat as an oxide. Some work has been carried out on the direct fusion of carbide materials in a sodium peroxide/sodium hydroxide fusion mixture.[8] This has been found to be especially useful for the complete dissolution of carbides containing chromium[9] and ruthenium.[10]

Nitrides. The nitrides of plutonium and uranium differ considerably in their behaviour on dissolution in mineral acids. Plutonium mononitride dissolves readily in hydrochloric acid with quantitative hydrolysis of the nitride radical to the ammonium ion, which can then be subsequently determined by the Kjeldahl method.[11] Uranium mononitride can only be dissolved with difficulty in hydrochloric acid with the addition of hydrofluoric acid, but again the Kjeldahl method is applicable.[12] There is therefore no difficulty in analysing binary mixtures of these two mononitrides. The higher nitrides of uranium ($UN_{1\cdot5-1\cdot7}$) are much less readily attacked by mineral acids, and complete dissolution is only obtained after prolonged treatment with hydrochloric acid plus hydrofluoric acid in the presence of sodium selenate or potassium chlorate, or with a mixture of phosphoric and sulphuric acids. This type of attack invariably results in low recoveries of nitrogen by the Kjeldahl technique, but it can of course be employed for the determination of the uranium content. A more satisfactory approach to the dissolution of the higher nitrides of uranium involves heating at 195° in hydrochloric acid in a sealed tube,[13] since under these conditions no loss of nitrogen occurs.

Phosphides. The behaviour of phosphides of uranium towards acid dissolution is similar to that of the nitrides. There is a tendency to lose phosphine if the dissolution is not carried out carefully,[14] and the higher phosphines are much more resistant to acid attack. In all cases a more satisfactory approach is to sinter the sample in a 3:1 mixture of sodium peroxide and sodium carbonate, and then to extract the melt with dilute nitric acid.

Silicides. The silicides of uranium and plutonium can be readily dissolved in hydrochloric acid with the addition of hydrofluoric acid to disperse the silica, and this approach is suitable for the determination of the metallic contents. Alkaline fusion and alkaline peroxide sintering of these silicides are unsatisfactory, resulting in losses of silicon as silane or incomplete dissolution at the acid leaching step. Satisfactory results can be obtained if the silicides are first oxidized by ignition in air.[15,16]

The addition of the elements molybdenum, iron, chromium, cerium and ruthenium to the ceramic systems discussed above has not created any additional dissolution difficulties and the relevant information is included in Table I.

Methods of separation in the analysis of ceramic materials

Owing to the difficulties inherent in handling radioactive materials in glove boxes, chemical separations are avoided whenever possible, but, if unavoidable, ion-exchange or chromatographic techniques are preferred because of the simplicity of the apparatus required. The anion-exchange separation of quadrivalent plutonium from uranium, iron, molybdenum, cerium and many other elements, in $8M$ nitric acid, has been widely used[17–20] with satisfactory results. The technique is eminently suited to the separation and concentration of plutonium before its determination by spectrophotometric measurement.[21,22] Careful attention must be given to the adjustment of the oxidation state of the plutonium before passage of the solution through the ion-exchange column, and details of the procedure used have been given.[9] Difficulty has been experienced in attempting to apply controlled potential coulometry to solutions after anion-exchange separations. Degradation products from some ion-exchangers resist oxidation in solution and then interfere in the coulometric procedures by poisoning the platinum working electrode.[23] Cation-exchange separation has also been used to separate plutonium(III) from silicate solution,[16] and to remove uranium(VI) from phosphate solution.[14] Reverse-phase partition chromatography with tri-n-butyl phosphate(TBP) supported on Kel-F has been employed for separating plutonium and uranium from iron. It has been shown to be a suitable technique of separation before the controlled potential coulometric determination of plutonium.[23] General application of this technique has been restricted, however, because of changes from batch to batch in the surface characterization of the Kel-F leading to variations in the amount of absorbed TBP. Solvent extraction techniques, particularly those employing volatile combustible solvents, are undesirable in the confined volume of a radioactive glove box, and hence have been avoided whenever possible. The separation of ruthenium as the tetroxide from plutonium and uranium by extraction into carbon tetrachloride has, however, been found preferable to separation by distillation from perchloric acid solution.[10]

Methods of determination, metallic constituents

The main constituents of most of the ceramic materials for analysis are uranium and plutonium, and these elements may be determined by a variety of methods.

TABLE I.—THE DISSOLUTION OF PLUTONIUM AND URANIUM CERAMIC MATERIALS

Material	Mineral acids	Alkaline fusion	Ammonium bisulphate fusion	High temperature/high pressure dissolution
PuO_2	Dissolve in HNO_3/HF (dissolves with difficulty).	Sinter at 400°C (*a*) or fuse at 600°C (*b*) in 1:1 Na_2O_2/NaOH. Extract into HCl.	Fuse at 400°C (*c*) for 4 hr. Extract into H_2SO_4.	
PuO_2/UO_2	Dissolve in 8*M* HNO_3, if in solid solution.		Fuse at 400°C (*c*) for 4 hr. Extract into H_2SO_4.	
PuC, UC, PuC/UC	Dissolve in mineral acids, (organic deposits are formed).	Fuse at 600°C (*b*) in 1:1 Na_2O_2/NaOH. Extract into mineral acid.	Ignite to oxide and treat as PuO_2/UO_2 (*c*)	
PuN	Dissolve in mineral acids	Hydrolyses readily in aqueous alkali.		
UN, PuN/UN	Dissolve $UN_{\leq 1\cdot 5}$ in HCl/HF (there is no loss of N_2) Dissolve $UN_{1\cdot 5}$ in HCl/HF in the presence of oxidizing agents (there is some loss of N_2)			$UN_{<1\cdot 5}$ dissolve in HCl. $UN_{>1\cdot 5}$ dissolve in HCl/HF.
UP, U_3P_4	Dissolve in HCl/HNO_3, (there is loss of PH_3).	Sinter at 350°C (*d*) in 3:1 Na_2O_2/Na_2CO_3. Extract into HNO_3.		
USi	Dissolve in HCl/HF (there is some loss of Si)	Ignite to oxide, fuse with Na_2CO_3 (*d*). Extract with HCl.		
PuSi, PuSiC	Dissolve in HCl/HF, (there is some loss of Si).	Ignite to oxide. Sinter in 1:1 Na_2O_2/NaOH (*a*). Extract into HCl.		
(Pu, U)C–Fe	Dissolve in 8*M* HNO_3. Evaporate to fumes with H_2SO_4 to destroy organic residues.			
(Pu, U)C–Mo	Dissolve in 6*M* HCl + HNO_3 (organic residues are formed)			
(Pu, U)C–Cr		Sinter at 400°C (*a*) with 1:1 Na_2O_2/NaOH. Extract in HNO_3		
(Pu, U)C–Ce	Dissolve in 8*M* HNO_3. Evaporate to fumes with H_2SO_4.			
UC–Ru		Fuse at 600°C (*b*) in 1:1 Na_2O_2/NaOH		

(*a*) Pt crucible

(*c*) Pyrex vessel

Owing to the radioactive nature of the samples, we have concentrated on methods that need only limited handling of the sample, or its solution, in glove-box or fume-cupboard facilities. Preference has been given to methods possessing some degree of specificity for uranium or plutonium, together with reasonable sensitivity and adequate precision. The methods selected are summarized in Table II and comments on our experiences with these methods are as follows.

Plutonium. The spectrophotometric determination of plutonium(III) by absorptiometric measurement at 565 mμ is preferred for the analysis of systems containing only plutonium and uranium (*e.g.*, PuO_2/UO_2, PuC/UC or PuN/UN). For samples containing more than 10% plutonium the determination can usually be carried out without separation from uranium, but the measurement must be made differentially in order to obtain adequate precision for the determination.[21,22] For samples containing 1–10% plutonium, either a separation must be carried out, or the appropriate amount of uranium must be added to the plutonium standard solutions employed in the differential measurement. A quantity of 25–50 mg of plutonium is required for each determination, and the operations of dissolution, oxidation-state adjustment and absorptiometric measurement must all be carried out in glove boxes.

Redox methods are more convenient for the precise analysis of samples containing smaller amounts of plutonium in the presence of other constituents in addition to uranium. Controlled-potential coulometry is a very suitable technique and we have used it for the analysis of sample aliquots containing about 5 mg of plutonium in the presence of uranium,[23] chromium[9] and cerium.[30] A coefficient of variation of ±0·25% is obtained on using the oxidation-reduction of the Pu^{3+}/Pu^{4+} couple at a platinum working electrode. Unfortunately iron interferes in this determination owing to the proximity of the E° value of the Fe^{2+}/Fe^{3+} couple. Attempts have been made to overcome this interference by the use of complexing agents. In principle this can be done by complexing the iron with 1,10-phenanthroline at pH 2·0 before carrying out the plutonium determination. In practice the presence of 1,10-phenanthroline in solution causes low recoveries for plutonium to be obtained, by poisoning the platinum working electrode.[23] However, it has recently been reported that this effect is not obtained with a gold electrode.[24] Plutonium can be determined by a redox method in the presence of iron provided that the determination is based on the PuO_2^{2+}/Pu^{4+} couple. It has been found more convenient by the authors to carry out this determination by means of a potentiometric titration, although a controlled-potential coulometric method has been reported.[28] The potentiometric titration has been used for the accurate determination of plutonium with a precision of better than 0·20% (coefficient of variation) for about 5-mg amounts of plutonium or less. This method is particularly useful after the dissolution of plutonium-containing ceramic materials by fusion with ammonium hydrogen sulphate.[4]

Uranium. Although a differential spectrophotometric method is available for the determination of uranium, it is not very attractive since a uranium concentration of 40 mg/ml is required for each determination. Redox methods of analysis possess more desirable features. For example, the controlled-potential coulometric determination of uranium by reduction of UO_2^{2+} to U^{4+} at a stirred mercury pool[29] is now an established technique, and it can be used in the presence of cerium, chromium, plutonium and iron. We have experienced some difficulty with the use of U_3O_8 as a standard material as compared with absolute electrical calibration. Recoveries of 100·5% were obtained relative to the quantity of U_3O_8 taken. However, this discrepancy does not arise on taking pure uranium metal as a standard material, and accurate determinations may be carried out on 5–10 mg of uranium with a precision of 0·25% (coefficient of variation).

Molybdenum. The differential spectrophotometric determination of molybdenum by absorptiometric measurement of its thiocyanate complex at 500 mμ following anion-exchange separation from plutonium has been employed with satisfactory results in the analysis of (Pu, U)C–Mo samples containing up to 10% w/w of molybdenum. Conversion of this carbide into its corresponding oxide by ignition is undesirable because of the probable loss of molybdenum by volatilization. The direct dissolution of this carbide in hot $8M$ nitric acid, in order to minimize the formation of organic products, tends to encourage the precipitation of molybdenum as a hydrated oxide. This difficulty can be overcome by starting the dissolution with hydrochloric acid, followed by the addition of $8M$ nitric acid. This procedure results in the formation of both soluble and insoluble organic matter, but this does not interfere with the adjustment of the oxidation state of the plutonium nor with the anion-exchange separation. Some organic material is retained by the ion-exchange column, and the remainder is destroyed by oxidation with a mixture of nitric and sulphuric acids as a preliminary to the formation of the molybdenum thiocyanate complex. The final absorptiometric measurement can be carried out in the presence of uranium with a precision of 0·5% (coefficient of variation).

Ruthenium. Spectrophotometric methods are the most suitable for the determination of minor quantities (<1 mg) of this element. Ruthenium has been determined in UC–Ru and (Pu, U)C–Ru samples by measurement of a chloro-complex of ruthenium(IV) at 485 mμ after a solvent extraction separation. Carbide samples are first dissolved by fusing with sodium peroxide/sodium hydroxide at 600° in an alumina crucible. The cooled melt is extracted with water and the resulting solution is acidified with hydrochloric acid. The ruthenium is oxidized to the quadrivalent state with sodium hypochlorite before extraction with carbon tetrachloride. After back-extraction into sodium hydroxide solution containing sodium bisulphite, the solution is acidified with hydrochloric acid and heated to 100° to produce a stable chloro-complex of ruthenium. The absorbance of this complex is measured at 485 mμ and a correction made for any slight losses of ruthenium occurring in the separation process, on the basis of a ruthenium-103 tracer measurement.[10] The precision of the ruthenium determination in this type of sample is ±0·5% (coefficient of variation). During investigations into the nature of the ruthenium chloro-complex produced by fusion with sodium peroxide and hydroxide, it was noted that the acid solution could be reduced and decolourized at a potential of +0·05 V *vs.* the S.C.E. with a platinum electrode. This reduction, which was irreversible, corresponded to a 1-electron change, and could be used for the controlled-potential coulometric determination of ruthenium in the presence of uranium, but not in the presence of plutonium. The precision obtained was ±1·6% on 1–4 mg of ruthenium.

Iron. Controlled-potential coulometry is suitable for the determination of 1–10 mg amounts of iron in $0{\cdot}5M$ sulphuric acid solution with a precision of 0·1%, and in the presence of uranium. Although the technique cannot be applied directly to the determination of iron in (Pu, U)C–Fe cermets it can be used to determine the total Fe + Pu based on the Fe^{2+}/Fe^{3+} and Pu^{3+}/Pu^{4+} couples. The plutonium content is then determined independently by the potentiometric titration based on the reduction of Pu(VI) to Pu(IV), and the iron content is obtained by difference.[25]

Cerium. Redox methods are very suitable for the determination of this element, and cerium(IV) can be reduced coulometrically at the platinum electrode at a potential of +0·90 V *vs.* the S.C.E. This reduction can be carried out in the presence of uranium and plutonium provided that both elements have been previously oxidized to their highest oxidation states. Silver(II) oxide is used to oxidize the cerium to the quadrivalent state and the plutonium and uranium to the sexivalent state. Excess of oxidant is readily destroyed by adding sulphamic acid to the cold solution. This procedure has been applied to a solution of (Pu, U)C–Ce prepared by dissolution in hot $8M$ nitric acid, followed by evaporation to fumes of sulphuric acid. Cerium has been determined on an aliquot of this solution, containing 1–2 mg of cerium, with a precision of ±0·25% (coefficient of variation).[19]

Methods of determination, non-metallic constituents

The choice of methods available for the analysis of the non-metallic constituents of the ceramic materials quoted above is not nearly so wide as that for the metallic ones. Furthermore, although the non-metallic content of the carbides, nitrides, phosphides and silicides of uranium and plutonium is low at between 5 and 15% w/w, the necessity to define the stoichiometry of the materials as clearly as possible calls for the use of methods of the highest precision and accuracy. There is therefore a tendency to select classical methods of analysis which can be used as reference methods in the development of more rapid instrumental techniques of analysis.

Carbon in carbides. All the standard methods of carbon determination involve combustion to carbon dioxide in a stream of oxygen followed by some technique for trapping the carbon dioxide before measurement of the quantity produced. In order to avoid segregation difficulties, a sample weight of 0·5–1·0 g was chosen so as to produce up to 100 mg of carbon dioxide on ignition. This quantity of carbon dioxide proved difficult to trap in aqueous reagents, and the gravimetric determination using solid absorbents was too time-consuming. Modification of the Cook and Speight equipment for measuring the pressure of the carbon dioxide produced proved to be relatively simple, and this modified apparatus gave precise results (coefficient of variation 0·3%) with a high sample throughout. The apparatus could also be conveniently arranged with the sample preparation and combustion inside a glove box and with the gas-handling and vacuum equipment situated in the open laboratory.[26]

Nitrogen in nitrides. Methods for the determination of nitrogen in nitrides involve conversion into ammonia, or release as nitrogen gas from the sample. Selection of a suitable technique for the analysis of uranium and plutonium nitrides is complicated by the range of stabilities of these materials, plutonium nitride being readily hydrolysed in moist air and the higher nitrides of uranium being extremely resistant to hot mineral acids. The most suitable methods of dissolution are summarized in Table I and further details are reported elsewhere.[12,13] When the complete dissolution of a nitride has been achieved, the distillation of the ammonia formed and its titrimetric determination present little difficulty. Under glove-box conditions, however, it has been found more satisfactory to displace the ammonia with argon rather than steam and a higher sample throughout can be maintained.[12] The Dumas method of nitrogen determination in which the nitride is converted into nitrogen gas, although useful as a reference method of analysis for the higher nitrides of uranium, does not appear to possess any special advantage and is extremely slow.[27]

Phosphorus. Work on the determination of phosphorus in heavy element phosphides has been restricted to the analysis of UP and U_3P_4. Details of the dissolution technique are given in Table I and the phosphorus was determined gravimetrically after precipitation as ammonium phosphomolybdate under carefully controlled conditions.[14]

Silicon. The determination of silicon in uranium/plutonium silicide and plutonium silicon carbide samples presented little difficulty. In all cases it was found necessary to oxidize by ignition in air at 850° in order to avoid losses of silane during dissolution.

TABLE II.—METHODS OF ANALYSIS OF PLUTONIUM AND URANIUM CERAMIC MATERIALS

Element	Quantity	Method of determination	Solution conditions	Precision	Comment
Pu	25–50 mg	Differential absorptiometry at 565 $m\mu$, 4-cm cells.	1*M* HCl, 5% NH_2OH, HCl	0·1%	No separation from U above 10% Pu
	1–10 mg	Controlled-potential coulometry	Pu^{3+}/Pu^{4+} in 1*M* H_2SO_4, E° + 0·50 V *vs.* S.C.E. Reversible	0·25%	No separation from U, Ce, Cr
	1–10 mg	Potentiometric titration	Oxidize with AgO, destroy excess, add excess of Fe^{2+}, back-titrate with Ce^{4+}	0·2%	No separation from U and Fe
U	5–10 mg	Controlled-potential coulometry	UO_2^{2+}/U^{4+} in 1*M* H_2SO_4, electrolysis − 0·325 V *vs.* S.C.E. Irreversible.	0·25%	No separation from Pu, Ce, Cr, Fe.
Ce	1–2 mg	Controlled-potential coulometry	Oxidize with AgO, destroy excess. Reduce at + 0·9 V *vs.* S.C.E.	0·25%	No separation from Pu and U
Mo	0·5 mg	Differential absorptiometry at 500 $m\mu$, 1-cm cells.	Molybdenum thiocyanate complex in 2*M* H_2SO_4	0·5%	Separation from Pu required
Ru	40 μg–1 mg	Absorptiometry at 485 $m\mu$	Quadrivalent chloro-complex in 5·5*M* HCl	0·5%	Separation from Pu and U required
Ru	1–4 mg	Controlled-potential coulometry	5*M* HCl solution of the binuclear chloro-complex of ruthenium (IV). Irreversible reduction at + 0·50 V *vs.* S.C.E.	1·6%	No separation from U required
Cr	1 mg	Potentiometric titration	1*M* H_2SO_4. Oxidize with AgO, destroy excess, add excess of Fe^{2+} back-titrate with Ce^{4+}.	0·2%	
Fe	1–10 mg	Controlled-potential coulometry	Fe^{2+}/Fe^{3+} in 1*M* H_2SO_4. E° + 0·42 V *vs.* S.C.E. Reversible	0·10%	Separation from Pu required
C	25 mg	Manometric measurement of CO_2	—	0·30%	
N	5 mg	Kjeldahl	Hydrolysis in HCl/HF(UN), or NaOH solution (PuN), or sealed-tube dissolution for higher nitrides of uranium	0·5% 0·5% 0·9%	
N	5 mg	Dumas	—	0·5–1·0%	
P	10–15 mg	Gravimetric	Ammonium phosphomolybdate, dried at 250°C	0·2%	
Si	10–20 mg	Gravimetric	Quinoline silicomolybdate	0·5%	

The silicon was determined gravimetrically after precipitation as quinoline silicomolybdate. In the case of plutonium silicates a separation was carried out in order to avoid co-precipitation of plutonium with the quinoline silicomolybdate.[15,16]

POST-IRRADIATION ANALYSIS

During recent years several chemical methods have been developed for the determination of the burn-up, or the degree of irradiation, undergone by specimens in irradiation experiments. Moreover, these are readily applicable to small specimens of fuel (metal, oxide or carbide) after dissolution in mineral acids. For larger fuel elements or test specimens, however, the chemical methods are used in conjunction with gamma-scanning which is employed to determine the distribution of burn-up throughout specimens by indicating the distribution of selected radioactive fission products.[31] Gamma-scanning aids in the location of areas from which samples should be taken for chemical burn-up analysis.

Some confusion has existed over the definition of burn-up, but the definition considered by us to be the most meaningful is expressed as follows:-

$$\text{Atom \% burn-up} = \frac{F_t \times 100}{N_t^\circ} \tag{1}$$

where F_t is the total number of fission events that have occurred during the irradiation, and N_t° is the total number of atoms of atomic weight greater than 225 present in the sample before irradiation. In order to use equation 1, it is necessary to determine F_t and N_t° for each sample, and various methods of doing this have been developed and investigated. The chemical methods for F_t measure the total number of fissions by determining the quantity of a fission product (stable or radioactive), or by measuring the change in the isotopic composition of the heavy elements in the fuel. N_t° can be determined in metals and stoichiometric compounds by simply weighing the sample. This approach is very limited, however, and it is inapplicable to more complex fuels containing inert diluents and mixtures of fissile materials. This difficulty is overcome by determining the total number of heavy atoms present, after irradiation, by chemical means. The burn-up of material, where significant burn-up has occurred, is then calculated by using the following modified form of equation 1:

$$\text{Atom \% burn-up} = \frac{F_t \times 100}{N_t + F_t} \tag{2}$$

when N_t is the total number of atoms of atomic weight greater than 225 in the sample after irradiation.

At A.E.R.E. the isotopic dilution method of analysis is used extensively for the determination of the uranium and plutonium contents of irradiated fuels. This technique employs a solid source mass spectrometer, and it is probably the most accurate and precise method of determining these elements at the microgram level. Precision and accuracy data have been reported by Webster and co-workers.[32,33] By working at the microgram level, safety and handling problems in the subsequent chemical isolation of uranium and plutonium are reduced to a minimum. Even so, shielded cells and other special facilities are essential for the initial dissolution procedures.[34]

The determination of the total number of fission events (F_t)

The chemical methods available for the determination of the total number of fission events can be classified as (1) methods based on fission products (stable and radioactive); (2) methods based on the isotopic analysis of the fissile material before and after irradiation. These methods are now well established and they are considered in greater detail in the remainder of this section.

Fission product methods

Stable fission-product nuclide method. There are several factors that dictate the choice of a nuclide for use as a measure of the number of fissions taking place during the irradiation of a specimen. The requirements of a stable fission product nuclide can be summarized as follows.

(*a*) It must occur near the peaks of the fission yield curves. This minimizes errors due to variations in fission yield with neutron energy and fissile nuclide. Enough of the fission product must be produced for mass spectrometry without excessive amounts of highly radioactive samples having to be taken for analysis.

(*b*) Preferably there should be at least one other stable isotope which is not produced, or only produced in very small amounts, in fission. Determination by the mass spectrometric isotopic dilution method is then possible.

(*c*) It must have a low capture cross-section for neutrons for itself and its precursors.

(*d*) Its volatile precursors, if any, must be short-lived and remain in the specimen.

(*e*) It must be easily separated on a carrier-free basis from radioactive species.

(*f*) It must not occur in significant amounts in the un-irradiated samples, or be picked up in subsequent chemical separations.

Molybdenum and neodymium are two elements with isotopes which meet most of these requirements.[35] Molybdenum has four stable isotopes produced in high yield during fission, namely isotopes 95, 97, 98 and 100. The naturally-occurring isotopes (92, 94 and 96) are not produced in any significant quantity in fission and isotope 92 can conveniently be used as a tracer isotope for isotopic dilution analysis. Isotopes 94 and 96 can be employed to indicate any contamination by natural molybdenum. Neodymium has six stable isotopes which are produced in usable amounts in fission, isotopes 143, 144, 145, 146, 148 and 150. Naturally-occurring neodymium-142 is not produced in fission and can be used as a tracer for isotopic dilution analysis. The precursors that do exist are of short half-life and of low neutron-capture cross-section. The neutron-capture cross-sections of the neodymium isotopes are insignificant except for isotope 143, which is about 300 barns. It is not considered advisable to use neodymium-144 unless the sample has undergone a very long period of cooling (8–10 years) because of the long half-life of cerium-144 (285 days).

Although both molybdenum and neodymium meet the necessary requirements for isotopic dilution analysis, it has been possible to arrive at certain conclusions regarding the usefulness of these methods from experience in applying them to many types of samples, including metals, cermets, oxides and carbides. Undoubtedly the neodymium method has proved to be the one that is most widely applicable to different types of sample. The only difficulty has occurred on applying the method to very low burn-up samples after short cooling times. With such samples the amount of neodymium in the sample is so small that large sample weights have to be handled in $\alpha\beta\gamma$ cells in order to recover enough material for subsequent mass spectrometry. The molybdenum method, on the other hand, must be restricted to low temperature irradiations of fuels because molybdenum has been found to form compounds with ruthenium, rhodium and technetium fission products. This effect increases with temperature and time. These compounds are insoluble in the mineral acids normally used to dissolve irradiated samples. In addition to this problem of insolubility, solutions of molybdenum in nitric acid are not very stable over a period of time. Also the contamination of samples with the naturally-occurring elements is a much greater problem with molybdenum than with neodymium. In particular, there is serious contamination from molybdenum present in steel which is used as a cladding material.

In view of the considerations above, much greater emphasis has been given to the application of the neodymium method to the analysis of irradiated samples. The tracer nuclide used in this work is electromagnetically-enriched neodymium-142. In using this method it is desirable to separate the neodymium from other sample constituents, so as to prevent interference from ions of similar mass numbers and to stop contamination of the mass spectrometer with radioactive materials. Full details of the method of separation developed in this laboratory are to be published in the near future.[36]

The stable fission-product method is capable of a high overall accuracy because it is dependent only on the tracer calibration and the fission yield. It is not dependent on a knowledge of the fission rate or the time of irradiation of the specimen. Results agreeing to better than ±2% have been obtained for almost all levels of burn-up, where careful control has been exercised in the chemical separation of the neodymium and in the subsequent mass spectrometry. The high precision that can be achieved is inherent in the isotope dilution technique.

Radioactive fission-product nuclide methods. There are a number of radioactive fission-product nuclides available for the determination of the total number of fission events. The final choice of nuclides best suited for this purpose has been on the basis of length of half-life and ease of measurement of the emitted radiation. The chosen nuclide must fulfill the following conditions.

(*a*) It must have a high gamma-ray abundance and fission yield for good sensitivity. Fission-product nuclides produced in high yield are also less dependent on changes in the incident neutron energy.

(*b*) It must have a low neutron-absorption cross-section, and both the nuclide and its precursors must have a low volatility.

(*c*) It must have a half-life at least as long as the time of irradiation. A short-lived fission product would not adequately record changes in fission rate that occurred early in a long irradiation.

For most burn-up determinations the factors above limit the choice to the fission-product nuclides zirconium-95, cerium-144 and caesium-137 and these are considered individually in more detail as follows.

Zirconium-95. In most samples received for burn-up analysis, zirconium-95 and niobium-95 are the major gamma-ray emitters, producing a single composite photopeak at 0·75 MeV with a sodium iodide detector. Fortunately this peak can be resolved into the following components by using a lithium-drifted germanium detector—a photopeak at 0·724 MeV for zirconium-95 and a partially resolved peak at 0·756 MeV for zirconium-95 and at 0·764 MeV for niobium-95. A spectrum of this pair of nuclides is shown in Fig. 1.

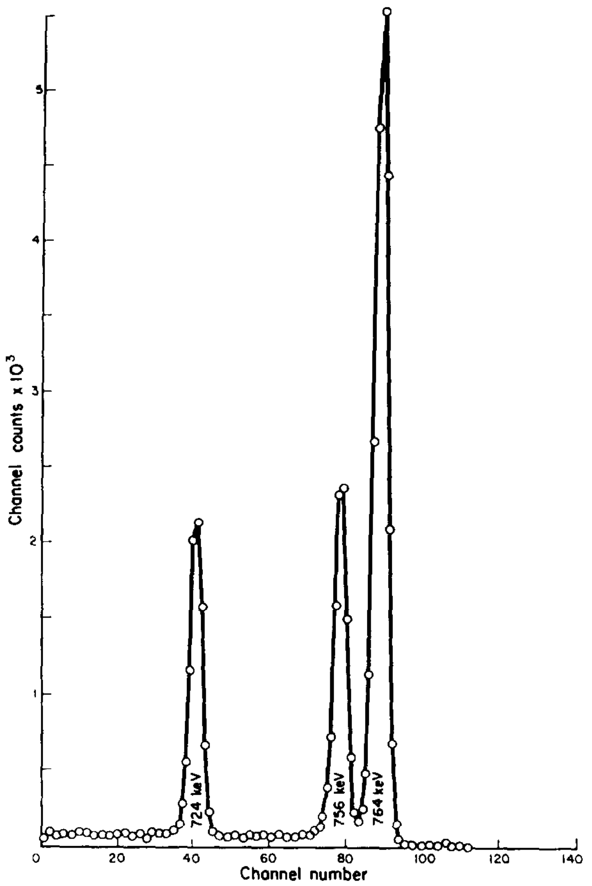

Fig. 1.—Gamma spectrum of $^{95}Zr/^{95}Nb$.

In order to calculate burn-up from an activity measurement using this pair of nuclides, it is necessary to know the contribution of zirconium-95 alone. This presents no problem if the germanium detector is used. However, there are difficulties with the sodium iodide detector since the contribution from zirconium-95 must be calculated from a knowledge of the irradiation history of the sample. This increases the uncertainty of the determination. Another difficulty arises from the comparatively short half-life of 65 days for zirconium-95. Despite these limitations, zirconium-95 is the only practical monitor for several irradiation conditions (see Table III).

When a sodium iodide crystal is used, then a radiochemical separation of zirconium-95 is essential. The chemical method for the separation of zirconium-95 from uranium, plutonium and fission products, before gamma-spectrometry, is based on the preliminary precipitation of zirconium as barium zirconyl fluoride.[37] After dissolution of this precipitate, the zirconium is precipitated as its mandelate which is finally slurried onto a counting tray with acetone. The tray is dried for 20 min in an oven at 130°. It is then cooled, weighed and counted.

Cerium-144. The two major gamma-active isotopes of cerium produced in fission are cerium-144 with a half-life of 285 days giving a γ-peak at 0·134 MeV, and cerium-141 with a half-life of 32 days giving a γ-peak at 0·145 MeV. The chemical properties

TABLE III.—CHOICE OF BURN-UP METHOD

Nature of material under irradiation	Low burn-up, 0–0·5%		Medium burn-up 0·5–10%		High burn-up, greater than 10%	
	Irradiation time		Irradiation time		Irradiation time	
	Short 10–20 days	Long >200 days	Short	Long	Short	Long
Low enrichment uranium 0·7–5% ^{235}U	$(Nd)^1$,Zr	Cs,$(Ce)^3$ $(Nd)^1$	Nd,$(Zr)^4$	Nd,$(Cs)^5$		
Medium enrichment uranium 5–60% ^{235}U	$(Nd)^1$,Zr	Cs,Ce $(Nd)^1$	Nd,Ce,$(Zr)^4$	Nd,$(Cs)^5$	IAD IAC ↔ $(Nd)^6$	
High enrichment uranium 60–93% ^{235}U	$(Nd)^1$,Zr	Cs,Ce, $(Nd)^1$	Nd,Ce,$(Zr)^4$	Nd,$(Cs)^5$	IAD IAC ↔ $(Nd)^6$	
Plutonium-239	$(Nd)^1$,Zr	Cs,Ce, $(Nd)^1$	Nd,Ce,$(Zr)^4$	Nd,$(Cs)^5$	IAD IAC ↔ $(Nd)^6$	
Low enrichment uranium plus plutonium	$(Nd)^1$,Zr^2	Cs,$(Ce)^3$ $(Nd)^1$	Nd,Ce,$(Zr)^4$	Nd,$(Cs)^5$	IAD IAC ↔ $(Nd)^6$	
Medium and high enrichment uranium plus plutonium	$(Nd)^1$,$(Zr)^2$	Cs,$(Ce)^3$ $(Nd)^1$	Nd,$(Ce)^3$,$(Zr)^4$	Nd,$(Cs)^5$	IAD IAC ↔ $(Nd)^6$	

IAD = Heavy element isotopic analysis based on the the depletion of the major isotope, and nuclear data.

IAC = Heavy element isotopic analysis based on the capture products, and nuclear data.

Brackets are used to denote those methods that are less suitable.

Notes on Table III

1. Neodymium method can be difficult to apply owing to excessive radioactivity.
2. Allowance must be made for the difference in fission yields of ^{95}Zr from ^{235}U and ^{239}Pu fissions.
3. Allowance must be made for the difference in fission yields of ^{144}Ce from ^{235}U and ^{239}Pu fissions.
4. Short irradiation to a moderate burn-up usually involves a highly rated fuel and consequent high temperatures. This results in the zirconium becoming difficult to dissolve by conventional methods.
5. Applicable to samples that have not exceeded 600°C in temperature.
6. The neodymium method has been found to give results which differ from the heavy element isotopic composition method at burn-up values in excess of 25%. This difference has not yet been resolved but it is considered that the IAD and the IAC results are correct.

of cerium-144, together with its half-life, combine to make it an attractive nuclide for the determination of the burn-up of metal and oxide samples. However, the presence of cerium-141 in samples of less than 200 days cooling makes the determination of cerium-144 very difficult with sodium iodide detectors. Fortunately the γ-peaks for cerium-144 and cerium-141 can be resolved with a lithium-drifted germanium diode, and this approach is used to overcome this difficulty. In the absence of this detector, it is possible to use a sodium iodide detector to measure the 2·18-MeV γ-peak of the praseodymium-144 daughter which quickly reaches equilibrium with the parent. However, the low abundance of this γ-peak, combined with the low efficiency of detectors at this high energy, reduces the precision of the measurement.

The method employed for the separation of cerium-144 before counting, is based on the oxidation of cerium with sodium bromate in 10*M* nitric acid, followed by extraction into isobutyl methyl ketone.[38] The cerium is recovered by shaking the organic layer with aqueous peroxide. It is then precipitated as its oxalate, filtered off and ignited to oxide at 800°. The oxide is finally slurried onto a weighed aluminium tray for counting.

Caesium-137. The γ-peak for caesium-137 occurs at 0·66 MeV, and it is potentially a good fission monitor for long irradiations. However, this system has some difficulties which should be appreciated. Several isotopes of caesium are produced in high yield in fission, including the stable isotope caesium-133. This particular isotope has an appreciable capture cross-section for neutrons, which can be greatly enhanced under certain reactor conditions by a very large resonance in its capture cross-section at $\sim$6 eV. Caesium-134 is the product of this n, γ reaction, and it has a half life of 2·3 years. It gives a complex gamma spectrum with γ-rays of high abundance at 0·605 and 0·796 MeV respectively, which interfere with the 0·66 MeV peak for caesium-137 when the sodium iodide detector is used. Fortunately, these peaks are well separated from each other with the lithium-drifted germanium diode, and the determination of caesium-137 from this spectrum presents no difficulties. The radiochemical separation of caesium from other fission products involves precipitation of caesium perchlorate, scavenging with ferric hydroxide and then precipitation of caesium chloroplatinate.[39]

A disadvantage in the use of caesium-137 for burn-up analysis arises from the fact that caesium migrates at relatively low temperatures. This unfortunately excludes its application to samples where the temperature is known to have exceeded 650° during the irradiation, though it is very satisfactory for the analysis of fuels where the temperature of the specimens is known to have been kept low below this temperature. Large scale migration of caesium-137 has been observed in this laboratory with fuels which have exceeded a temperature of 650°, and some caesium has been shown to leave the surface of the fuel under these circumstances.

The cerium-144 nuclide has proved to be a very reliable burn-up monitor. No evidence has been obtained for the migration of cerium and this is not surprising in view of the refractory nature of compounds of cerium. There is some evidence of solid solution formation of cerium and rare earths in UO_2 and UO_2/PuO_2 specimens. This nuclide has been used for burn-up determinations on many types of fuels (metals, oxides and carbides) with irradiation times up to approximately 2 years. With mixed fuels containing uranium-235 and plutonium-239 allowance has to be made for the fact that the fission yields for cerium-144 are significantly different for these two fissile materials. Without this correction a decrease in accuracy results.

The zirconium-95 nuclide is a reliable burn-up monitor for materials that have undergone short irradiations. The fission yields for this nuclide are significantly different for uranium-235 and plutonium-239, and allowance must be made for this in those cases where the ratio of U/Pu fission is known.

In general the radioactive fission product methods are relatively inexpensive to carry out, but they are dependent on the availability of an irradiation history for each specimen. Determinations by high-resolution gamma spectrometry on dissolved samples are capable of a precision of measurement of $\pm 2\%$ for the gamma rays, and an overall accuracy of about $\pm 5\%$ for the burn-up values under favourable conditions. This difference is explained by inaccuracies in the nuclear data available for the calculations. Although these methods are less accurate than the stable fission product methods, they have the merit of being quick to carry out.

Isotopic analysis methods

Changes in the isotopic composition of the uranium which occur during irradiation can be used for the burn-up analysis of uranium-base materials. It is usual to measure the depletion of the uranium-235 isotope and the growth of the uranium-236 isotope by mass spectrometry. This technique gives atom ratios, and the calculations involve the use of equations which relate the total number of uranium-235 fissions to the atom ratios before and after irradiation.

In the case of the depletion of uranium-235, the equation most commonly used is

$$F_5 = N_8^\circ[R^\circ_{5/8} + R^\circ_{6/8}) - (R_{5/8} + R_{6/8})]$$

where F_5 is the total number of ^{235}U fissions
N_8° is the total number of ^{238}U atoms present before irradiation
$R^\circ_{5/8}$ is the ^{235}U to ^{238}U atom ratio before irradiation
$R_{5/8}$ is the ^{235}U to ^{238}U atom ratio after irradiation
$R^\circ_{6/8}$ is the ^{236}U to ^{238}U atom ratio before irradiation
$R_{6/8}$ is the ^{236}U to ^{238}U atom ratio after irradiation

For calculations from the growth of ^{236}U, the following equation relating ^{235}U fissions to the ^{236}U/^{235}U ratios has been derived:

$$F_5 = N_5^\circ\left[\frac{R_{6/5} - R^\circ_{6/8}}{R_{6/5} + \alpha_5(1 + R_{6/5})}\right]$$

where F_5 is the total number of ^{235}U fissions
N_5° is the total number of ^{235}U atoms present before irradiation
$R^\circ_{6/5}$ is the ^{236}U to ^{235}U atom ratio before irradiation
$R_{6/5}$ is the ^{236}U to ^{235}U atom ratio after irradiation
α_5 is the capture to fission cross-section ratio for ^{235}U.

The total number of ^{238}U and ^{235}U atoms can be determined at the same time as the atom ratios by isotopic dilution mass spectrometry using ^{233}U as the tracer. Since all the isotopes of uranium can be measured on the mass spectrometer by scanning the uranium region, the data for these equations and for the atom per cent burn-up calculation can be obtained simultaneously. It is necessary to carry out chemical separation of uranium from other radioactive species in order to eliminate the latter from the mass spectrometer and to reduce interferences. The chemical operations need not be quantitative at any stage. A sequential separation scheme is employed for this purpose. First plutonium is removed by using an anion-exchange procedure from 8*M* nitric acid solutions with plutonium in the quadrivalent state.[40] Then the fission products are separated by means of reverse-phase partition chromatography using TBP supported on Kel-F.[41] After further purification by precipitation, the uranium is finally mounted on the tungsten side-filament of the mass spectrometer bead.

This method possesses the following advantages.

(*a*) The chemical operations need not be quantitative, except for the quantitative addition of tracer if the total number of uranium atoms in the sample is to be determined. These operations are relatively simple to carry out, and the method can be applied on a routine basis.

(*b*) Only small quantities of material (μg) need be processed, thus enabling the majority of the work to be carried out without shielding.

The method also has some disadvantages, as follows.

(*a*) It is very sensitive to contamination by uranium of different isotopic composition. Thus clean and careful work is needed to prevent cross-contamination of samples.

(*b*) Samples of representative unirradiated materials are required to determine the isotopic compositions before irradiation. This information is needed in any case, however, by the reactor operator for reactor loading calculations.

(*c*) Accurate values for nuclear parameters, such as ratios of neutron-capture to fission cross-sections, are required.

The usefulness of the method depends on the amount of burn-up undergone by the sample. It is least accurate for low burn-up samples where the change in isotopic composition of the uranium is small, but it is most accurate for high burn-up samples of enriched material. The growth equation is useful over a wider range of conditions than the depletion equation.

General recommendations on the methods of burn-up analysis

During the last six years a large number of samples of irradiated nuclear fuel have been examined by these methods of burn-up analysis. The samples have come from test irradiation programmes, and they have varied in size from individual coated particles up to full-scale fuel elements from power reactors. The enrichment, the rating, the duration of the irradiation, the neutron spectra, as well as the burn-up levels, have varied very considerably.

As a result of this work it has now been found possible to make an assessment of the various methods and draw up a set of rules for the choice of the best method for the analysis of subsequent samples. These rules are intended only as a guide, since the number of samples to be analysed and the precision and accuracy required also have some influence on the method employed. If a meaningful result is to be obtained, the analyst must have access to certain information regarding the conditions of irradiation, such as temperature, rating, power cycling, proximity of control rods and other rigs, *etc.* A knowledge of the irradiation history and the neutron energy distribution is desirable. Archive material kept as a representative of each sample is also extremely useful.

Experience has been gained on materials irradiated in thermal reactors and fast reactors. All samples are first examined non-destructively by gamma-ray spectrometry using a lithium-drifted germanium detector, and specimens are scanned for integral burn-up and fission-product migration measurements. Small quantities of sample from specific positions on the fuel are then taken for subsequent destructive chemical analysis.

The recommendations in Table III are intended for use with material originating from an irradiation programme on test specimens and pieces of selected fuel elements, rather than for accountancy and reprocessing requirements. It is assumed that the highest accuracy and precision is required, consistent with the number of samples and time available for analysis. The recommendations apply equally to fast reactor and thermal reactor fuels, as far as our present knowledge goes, but they will possibly require amending later when more information becomes available. It must be appreciated, however, that burn-up determinations of materials irradiated in fast reactors suffer very much from the lack of fission-yield values in these neutron energy fluxes and from the lack of accurate capture and fission cross-section values at the positions of irradiation. At present the accuracy of a burn-up determination on material irradiated in a fast reactor is no better than ±15 %, irrespective of the chemical method employed.

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Zusammenfassung—Eine umfassende und kritische Übersicht über die analytischen Methoden in der Technologie der Kernbrennstoffe.

Résumé—Une revue générale et critique des méthodes analytiques en technologie des combustibles nucléaires.

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DETERMINATION OF THE PRECISE COMPOSITION OF THE TRIPLE SODIUM URANYL ACETATES OF MAGNESIUM, ZINC AND NICKEL, AND SOME OBSERVATIONS ON THE USE OF THE FIRST TWO COMPOUNDS FOR THE DETERMINATION OF SODIUM

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Summary—Three triple sodium uranyl acetates $NaM(UO_2)_3(CH_3COO)_9 \cdot nH_2O$ in which the bivalent metals M were magnesium, zinc and nickel, have been precipitated and the air-dried compounds analysed for uranium by a highly precise method. Despite contrary claims it has been established that the compounds are precise hexahydrates the maximum deviation of n from 6 in any one analysis being 0·1. The precipitation of sodium as the magnesium or zinc compound gives results which depend on the excess of the reagents, and positive errors can be obtained. It is also concluded that, contrary to the usual belief, the magnesium compound is rather less soluble than the zinc one and is therefore somewhat more sensitive for sodium determination.

A VERY large number of papers have been published on the determination of sodium by precipitation of compounds of the type $NaM(UO_2)_3(CH_3COO)_9 \cdot nH_2O$, where M is a bivalent metal, and the method in various forms—gravimetric, titrimetric and spectrophotometric—has found application to a wide range of materials but generally in circumstances requiring no better precision than about 1%. The work described in this paper was part of an investigation into the suitability of the triple acetate method for more precise sodium determinations. This work was abandoned because it was found that the fraction of sodium precipitated depended on the excess of reagents used and, for some unexplained reason, positive errors could be obtained. Certain definite conclusions could be drawn, however, some of which are at variance with opinions expressed by other workers. The most important aspect of the investigation forms the major subject of this paper and concerns the precise composition of three of the compounds of interest—those in which the bivalent metals were magnesium, zinc and nickel.

In view of the length of time that the method has been established it seems extraordinary that final agreement on the composition of these compounds has not been reached. While there is no doubt of the empirical formula $NaM(UO_2)_3(CH_3COO)_9 \cdot nH_2O$, varying values have been quoted for n in the compounds where M is Zn and Mg, the most widely favoured for determining sodium. The magnesium compound, dried for 30 min at 110°, was assigned 9 molecules of water by Streng,[1] but Caley and Foulk,[2] on the basis of an analysis for UO_2, Mg, Na and CH_3COO, decided that the water content corresponded to 6·5 molecules.

Barber and Kolthoff[3] assigned 6 molecules of water to the zinc compound and their careful investigation cannot easily be faulted. They washed the precipitate with portions of 95% alcohol (saturated with the compound), then with ether and dried it by suction. They showed that the product was stable when exposed for several days to atmospheres dried by calcium chloride or concentrated sulphuric acid. It was dehydrated completely in 2 hr at a pressure of 40 mbar and a temperature of 90–100°, and a further 2 hr gave practically no further loss in weight. At a temperature of 110° slow decomposition of the zinc salt proceeded beyond loss of water but the magnesium compound was found to be more stable and lost only 0·3% of its original air-dried weight in 20 hr at 110°.

The accuracies of the determinations of sodium in known quantities of pure sodium compounds in both of the investigations quoted above, indicated that the compounds being weighed were stable under the specified conditions and that the water contents were consistent with the formulae claimed within about 0·5 molecule.

Feldstein and Ward[4] showed that the air-dried nickel compound also contained a number of molecules of water close to 6 but stated that their analysis was not sufficiently accurate to decide between 6 and 6·5.

Despite the evidence indicating a composition approximating to the hexahydrate the original Streng formula for the magnesium compound with $9H_2O$ is still widely quoted in text-books, particularly general reference works on inorganic chemistry. Without any published experimental evidence the zinc salt is also quoted as containing $9H_2O$ in at least two books.[5,6] One of these gives the zinc compound with $9H_2O$ on one page and $6\frac{1}{2}$ H_2O on another but quotes a gravimetric factor for the latter which is actually correct for $6H_2O$.

Duval and Duval[7] claim that the triple acetates with zinc and magnesium are mixtures of hydrates and contain between 6 and 9 molecules of water, the water content increasing with decreasing temperature of precipitation. They give pyrolysis curves which show constant weight up to 75° in the case of the zinc salt and up to 91° in the case of magnesium. They state that the initial horizontal portion of each curve is the region of mixed hydrates, a statement which is contrary to the phase rule. In fact the horizontal affords good evidence for the existence of only a single hydrate over that particular temperature range.

The matter has been further complicated by the use of mixed aqueous-alcoholic solutions of reagents for determining sodium as the sodium magnesium uranyl acetate. Having used an aqueous-ethanolic reagent solution, Kahane[8] claimed that the precipitate contained 8 molecules of water but Caley and Rogers[9] showed that it contained about 1·5 molecules of ethanol and 4·5 molecules of water. Williams and Hains[10] used an aqueous isopropanol reagent solution and claimed that the magnesium triple salt so produced contained 7 molecules of water and 0·3 molecules of isopropanol.

Because of these uncertainties in the compositions of the triple acetates it was decided to carry out careful analyses of the three compounds in which the bivalent element was zinc, magnesium and nickel, to determine the number of water molecules with certainty. In such a case it is believed that the best method is to determine that constituent for which the most accurate analytical method is available, preferably using a method not requiring elaborate elemental separations. In the present instance the determination of uranium by a highly precise titrimetric procedure based on the oxidation of uranium(IV) to uranium(VI) was the obvious choice. The method used was based on a combination of well-tried standard methods and involved reduction of uranium(VI) to uranium(IV) in 1*M* sulphuric acid by amalgamated zinc in a Jones reductor, aerial oxidation of any uranium(III) to uranium(IV), addition of excess of iron(III), and titration of the iron(II) produced. Cerium(IV) sulphate was used as oxidant with ferroin as indicator, and was standardized against sodium oxalate. As it was required to establish the number of molecules of water in the compounds to within 0·05 or better, an error of not more than 0·05% was aimed at. Accordingly weight titration was used and the final step in both the standardization of cerium(IV) sulphate and the analysis of the triple acetate precipitates was back-titration with 0·02*M* iron(II).

As it had been shown that the fraction of sodium precipitated depended on the excess of reagent added, analyses were carried out on precipitates corresponding to more and less than 100% recovery to determine whether any of this effect was attributable to variations in the composition of the precipitate.

EXPERIMENTAL

Precipitation of Triple Acetates

Reagents

Precipitating solutions. Uranyl acetate solutions containing also zinc, magnesium or nickel acetate were prepared from analytical grade reagents and were made 1*M* with respect to acetic acid. They were saturated with the triple salt at room temperature and filtered immediately before use.

Standard sodium solutions. Solutions containing 3–6 mg of sodium per ml were prepared by weighing out analytical grade sodium chloride that had been ignited in a platinum crucible at 600–700°, dissolving it in water and diluting accurately to 250 ml.

Procedure

All precipitations were carried out at room temperature in stoppered glass test-tubes which were agitated for 30 min by rotation at about 20 rpm in a motor-driven shaker. Then 5-ml portions of standard sodium solution were delivered from a calibrated pipette to the tube and, if required, the solution was evaporated to dryness and the residue dissolved in the appropriate volume of water for the experiment. The measured volume of precipitating solution was added and, after shaking as described above, filtration was carried out on a weighed porosity 3 sintered glass crucible, and the precipitate was washed with a few ml of the precipitant and then with several portions of 95% alcohol saturated with the triple salt, a total of 25–30 ml being used. The precipitate was washed three times with a few ml of ether and dried by suction. The crucible and contents were weighed after standing for 20–30 min in the balance case, which contained no desiccant. The method was essentially that used by Barber and Kolthoff[8] and it was found that replicate determinations carried out under the same conditions generally agreed within 0·1–0·2%.

Determination of Uranium Contents of Precipitates

Reagents

Standard cerium(IV) sulphate, 0·2N in 1M sulphuric acid. This solution was prepared as described by Wilson and Wilson,[11] 110 g of ammonium hexanitratocerate (prepared by recrystallizing 99% pure material from dilute nitric acid) and 60 ml of concentrated sulphuric acid being heated to remove nitric acid and the residue dissolved and diluted to 1 litre with 1*M* sulphuric acid.

Iron(III), 0·4M. Prepared by dissolving 192 g of analytical grade ferric alum in 1*M* sulphuric acid and diluting to 1 litre with the same acid.

Standardization of cerium(IV) sulphate

The solution was standardized against approximately 0·5 g portions of analytical grade sodium oxalate which had been recrystallized from water and dried at 120°. The method was essentially that of Walden, Hammett and Chapman,[12] the cerium(IV) sulphate being delivered from a weight burette, with the quantities adjusted so that the oxalate was in slight excess. The solution was heated to about 50°, more cerium(IV) sulphate added until the solution was just yellow, the solution cooled to room temperature, 0·1 ml of 0·025*M* ferroin added, and the solution back-titrated with 0·02*M* iron(II) sulphate of which the titre against the cerium(IV) solution had previously been determined. The relative standard deviation of the mean of 3 titrations was 0·01%.

Procedure

The weighed precipitate (1–1·8 g) was dissolved in 50 ml of 1*M* sulphuric acid and reduced to uranium(IV) by passage through a Jones reductor as described by Kolthoff and Lingane.[18] After aerial oxidation of uranium(III) to uranium(IV) 20 ml of 0·4*M* iron(III) solution were added followed by 0·1 ml of 0·025*M* ferroin indicator, and the solution was titrated with the standard cerium(IV) solution, again delivered from a weight burette. The small excess of cerium(IV) was back-titrated with 0·02*M* iron(II) sulphate. A blank was also carried out and deducted from the observed titration.

RESULTS AND DISCUSSION

Table I shows the percentage of UO_2 found in each precipitate analysed, together with the recovery of the sodium added and the initial and final concentrations of UO_2^{2+} and M^{2+}. The concentrations in the mother liquor were calculated from the known volumes of the sodium and reagent solutions, the weight of precipitate, and the concentrations of the reagent solutions.

Three different magnesium uranyl acetate solutions were used, the first being that of Caley and Foulk[2] in which the uranyl concentration is low and which therefore requires a large volume of reagent per determination.

Two zinc uranyl acetate reagents were used, each containing the same concentration of zinc as Barber and Kolthoff's reagent. The uranyl acetate concentration of one solution was 1·10 times that of Barber and Kolthoff and that of the other 0·76 times.

One solution only of the nickel uranyl acetate reagent was used, that of Feldstein and Ward.[4]

The standard deviation of a single uranium determination corresponded to 0·03 molecules of water and the maximum deviation of the uranium content of any one precipitate from the theoretical for a hexahydrate corresponded to less than 0·07 molecules of water. The deviations from the theoretical hexahydrate values of the mean values for the three compounds were 0·01, 0·02, and 0·04 for the magnesium, zinc and nickel compounds respectively. It is clear, therefore, that the air-dried sodium uranyl acetates with magnesium, zinc and nickel are precise hexahydrates and that statements that have been made to the contrary are incorrect. The results for the uranium content of sodium copper uranyl acetate obtained by Caley and Rogers[9] also agreed very closely with the theoretical value for the hexahydrate and it is evident that $NaM(UO_2)_3(CH_3COO)_9{\cdot}6H_2O$, where M is a bivalent metal, constitutes as well-defined a class of compounds as the alums. It is difficult to account for the $6{\cdot}5H_2O$ found by Caley and Foulk[2] for the magnesium compound but their uranium figures appear to have been definitely low.

The variation in the fraction of sodium precipitated is clearly not due to any variation in composition of the precipitate and must be connected only with the excess of uranyl ion, bivalent metal and acetate in the mother liquor. When the standard technique of shaking for 30 min with small volumes of precipitant that was at least 0·15*M* in uranyl acetate was used, it was found that the apparent fraction of sodium precipitated increased with increasing excess of reagent from below 100% to a maximum of 100·6–100·8%. High sodium recoveries were also obtained in some experiments by Barber and Kolthoff;[3] Kolthoff and Lingane[13] obtained similar results, their gravimetric results being confirmed by titrimetric determinations of uranium. This phenomenon is difficult to explain. In the present work the precipitating solutions were shaken with excess of triple acetate and filtered just before use so that supersaturation could not have occurred. The only likely explanation appears to be the introduction of sodium from the glassware used, as it was observed that the triple

TABLE I.—DETERMINATION OF URANIUM CONTENTS OF $NaM(UO_2)_3(CH_3COO)_9 \cdot nH_2O$ WHERE M IS MAGNESIUM, ZINC OR NICKEL

	Volume of solutions		Molarity of solutions				Apparent recovery* of sodium added	UO_2 found in compound	Remarks
	Sodium	Reagent	Uranyl acetate		Bivalent metal acetate				
	ml	*ml*	Reagent	Mother liquor	Reagent	Mother liquor	%	%	
Mg	3·0	150	0·101	0·087	1·40	1·37	101·4	54·09	Allowed to stand overnight
	3·0	150	0·101	0·087	1·40	1·37	100·1	54·06	Shaken 1½ hours
	3·0	150	0·101	0·087	1·40	1·37	100·0	54·04	
	3·0	26	0·164	0·078	1·40	1·23	99·8	54·10	
	0·6	30	0·164	0·094	1·40	1·35	100·4	54·10	
	1·0	24	0·184	0·094	1·28	1·20	100·6	54·11	
	5·0	27	0·184	0·092	1·28	1·06	100·1	54·18	
							Mean % UO_2 found in all precipitates =	54·10	Std. devn. of means = 0·02
							Theoretical % UO_2 for $NaMg(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$ =	54·12	
Zn	1·0	50	0·168	0·099	1·28	1·23	99·5	52·73	
	1·0	50	0·168	0·099	1·28	1·23	99·6	52·66	
	1·0	35	0·241	0·139	1·28	1·21	100·3	52·63	
	1·0	35	0·241	0·139	1·28	1·21	100·3	52·67	
							Mean % UO_2 found in all precipitates =	52·67	Std. devn. of mean = 0·02
							Theoretical % UO_2 for $NaZn(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$ =	52·68	
Ni	1·0	30	0·145	0·078	0·71	0·66	98·9	52·96	
	1·0	30	0·145	0·078	0·71	0·66	98·6	52·95	
							Theoretical % UO_2 for $NaNi(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$ =	52·91	

* Assuming hexahydrate precipitated.

acetate deposited slowly from the filtered reagent on standing in glass bottles. Also, in the experiment in which 150 ml of the dilute reagent were used and precipitation carried on overnight in glass, a result of 101·4% was obtained. If this explanation is correct then results below about 100·7% obtained by the standard technique represent incomplete precipitation of the total sodium present. It would therefore appear that this system needs study with sodium-free apparatus—plastic or silica—and that excess of reagent should be such that results of at least 100·7% are obtained in glass. Future work could, with advantage, include determinations of the solubilities of the triple acetates in precipitating solutions and mother liquors, a tracer technique with sodium-22 or -24 being used.

The relative sensitivities of the zinc and magnesium reagents are of interest. It is usually considered[14] that the zinc reagent is the more sensitive of the two but that the magnesium reagent has the advantage of being less susceptible to interference by potassium. Such comparisons are generally misleading as they are between the Barber and Kolthoff[3] zinc reagent which is about 0·22*M* with respect to uranium and the Caley and Foulk[2] magnesium reagent with a uranium concentration of about 0·11*M*. Any differences therefore relate to the effect of uranium concentration rather than to the particular bivalent acetate used. Comparison should be made on the basis of equal uranium concentrations but it should be noted that even under these conditions Feldstein and Ward[4] claimed the zinc reagent to be the more sensitive in their qualitative tests. The present work does not support this view but indicates that the difference, while not very great, is somewhat in favour of the magnesium, *i.e.*, the solubility of the triple magnesium salt in a given reagent is less than that of the zinc salt in a reagent of corresponding composition. This is shown by the results in Table II.

TABLE II.—COMPARISON OF ZINC AND MAGNESIUM URANYL ACETATE SOLUTIONS AT SIMILAR CONCENTRATIONS FOR PRECIPITATING SODIUM

Molarity of reagent in mother liquor		Apparent recovery of sodium added, %	Molarity of reagent in mother liquor		Apparent recovery of sodium added, %
Uranium	Zinc		Uranium	Magnesium	
0·085	1·01	97·7	0·085	1·04	100·0
0·101	1·04	99·2	0·092	1·05	100·1
0·087	1·20	99·5	0·078	1·23	99·8
0·099	1·23	99·7	0·099	1·21	100·5

These experiments were not specifically designed for this comparison, so the reagent concentrations in the mother liquors from the zinc experiments do not correspond exactly to those in the magnesium experiments. Nevertheless the greater precipitation of the magnesium compound under similar conditions is quite clear. It is of interest to note that the zinc triple acetate is also more soluble in 95% alcohol than the magnesium one. Barber and Kolthoff[3] found 0·5 mg/ml for the solubility of the former and Caley and Foulk[2] 0·2 mg/ml for the latter.

Zusammenfassung—Drei ternäre Natriumuranylacetate $NaM(UO_2)_3(CH_3COO)_9 \cdot nH_2O$, in denen die zweiwertigen Metalle M Magnesium, Zink und Nickel waren, wurden gefällt und die an der Luft getrockneten Verbindungen mit einer sehr genauen Methode auf Uran analysiert. Entgegen abweichenden Angaben wurde festgestellt, daß die Verbindungen genaue Hexahydrate sind; die höchste Abweichung des n-Wertes von 6 in allen Analysen betrug 0,1. Die Fällung von Natrium als Magnesium- oder Zinkverbindung gibt Ergebnisse, die von dem Reagentienüberschuß abhängen; positive Fehler sind möglich. Es wird auch geschlossen, daß im Gegensatz zur herrschenden Meinung die Magnesiumverbindung beträchtlich unlöslicher als die Zinkverbindung und daher bei der Natriumbestimmung etwas empfindlicher ist.

Résumé—On a précipité trois acétates triples uranyl-sodium $NaM(UO_2)_3(CH_3COO)_9 \cdot nH_2O$, dans lesquels les métaux bivalents M sont le magnésium, le zinc et le nickel, et analysé les composés séchés à l'air pour l'uranium par une méthode hautement précise. Malgré des déclarations contraires on a établi que les composés sont des hexahydrates précis, la déviation maximale de n de 6 n'atteignant dans aucune analyse 0,1. La précipitation du sodium à l'état de composé du magnésium ou du zinc donne des résultats dépendant de l'excès des réactifs et l'on peut obtenir des erreurs positives. On conclut aussi que, contrairement à la conviction habituelle, le composé magnésien est quelque peu moins soluble que le zincique et est par conséquent un peu plus sensible pour le dosage du sodium.

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EFFECT OF CHROMIUM(III) AND OF OTHER IONS ON THE ABSORPTIOMETRIC DETERMINATION OF COPPER WITH 2,2′-BIQUINOLYL

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Summary—In the determination of small amounts of copper in certain alloys by liquid–liquid extraction of the bis-chelate of copper(I) with 2,2′-biquinolyl, recovery of copper has been reported to be low when chromium(III) is present. The adverse effect of chromium(III) could be overcome by adding iron(II). It is now shown that the inhibiting effect of chromium is attributable to the formation of a kinetically inert ternary complex of chromium(III), copper(II) and citrate ions containing an equal number of atoms of each of the two metals. Copper can be displaced from this complex by any of the transition cations Mn(II), Fe(II), Co(II), Ni(II) and Zn(II). Zinc is shown to form a ternary complex formally analogous to that of copper. The formation of the ternary complexes has been studied polarographically. The formation of binuclear complexes of various hydroxy-acids is reviewed and a probable structure for the ternary complex is proposed which explains its stability and kinetic inertness. Analogies are drawn between this complex and ternary complexes of UO_2(VI)–Al(III)–citrate and Cu(II)–Al(III)–tartrate which also cause interference in established analytical procedures.

The liquid–liquid extraction of copper(I) by 2,2′-biquinolyl (bq) followed by a spectrophotometric determination of the bis-chelate $Cu(bq)_2^+$ has been recommended by Hoste *et al.* for the determination of copper in water, animal tissues and blood plasma.[1] They extended the method, apparently successfully, to the examination of two "synthetic" steel solutions. However, when Elwell[2] applied Hoste's conditions to samples of stainless steels containing upwards of 5% chromium the procedure proved unsatisfactory, although if citric acid was present to prevent the precipitation of hydroxides it gave good results for carbon steels. Some typical results are shown in Table I.

Table I.—Determination of copper in steels[2]

Sample	Determination by Hoste's method as adapted by Elwell, %	Actual content, %*
Plain carbon steel 61A	0·104	0·10
Plain carbon steel 61B	0·086	0·09
B.C.S. No. 235 Stainless 18/8 (Ti, 0·6%; W. 0·7%)	0·75	0·98
B.C.S. No. 246 Stainless 18/12 (Mo, 2·9%; Nb, 0·8%)	0·05	0·13
B.C.S. No. 261, Stainless 18/12 (Nb, 0·7%)	0·03	0·06

* Certificate values or values previously determined.

While this investigation was proceeding, determinations of small amounts of copper in chromium salts containing very small amounts of iron were also being carried out. The results were variable and consistently low, but on one occasion when the chromium was in the tervalent condition, iron(II) was added to simulate the composition of a steel-sample and the recovery of copper was improved markedly. It was argued that while a large excess of iron(II) appeared to be necessary when a large amount of chromium was present this necessary large excess was not obtained in the unmodified method wherein the iron(III) solution is treated with hydroxylamine hydrochloride in the cold. With sample B.C.S. No. 246, reduction of the boiling solution gave 85% recovery of copper when hydroxylamine was used, but 100% recovery with hydrazine or sulphurous acid. On this basis, with sulphurous acid as the reductant in boiling solutions, a method was developed and applied successfully to a wide variety of steels.[2] In certain cases, and to ensure the presence of at least 40 mg of iron(II) in the final 17·5 ml of aqueous phase before extraction by the solution of biquinolyl in amyl alcohol, additional iron(II) sulphate was added at the appropriate stage [ref. (2), p. 513, Note (2)].

The chemistry of these remarkable observations has hithertoremained unexplained. The possibility that chromium(III) is acting as an oxidizing agent and thus diminishing the concentration of copper(I), and the possibility that the rôle of the iron(II) is that of a "holding reductant" would seem to be excluded by a consideration of the relevant oxidation-reduction potentials.[3]

$$Cu^{2+} + e \rightleftharpoons Cu^{+} \qquad E^0 = +0{\cdot}167\ V$$
$$Fe^{3+} + e \rightleftharpoons Fe^{2+} \qquad E^0 = +0{\cdot}771\ V$$
$$Cr^{3+} + e \rightleftharpoons Cr^{2+} \qquad E^0 = -0{\cdot}41\ V$$

A careful scrutiny of Elwell's paper elicited some possible points of difference, which might prove to be of significance, between the procedures he used in handling chrome steels and the procedures used by other workers when determining copper by the biquinolyl method. In the first place Elwell used citric acid to hold up the precipitation of the substantial amounts of iron when the solutions were buffered to a pH between 5 and 6 for the extraction stage. Secondly, sulphur dioxide was used as the reductant. Our preliminary experiments showed that in solutions free from iron(III) salts the reduction of copper(II) to copper(I) was quantitative when hydroxylamine was used, and as this reductant had been employed in earlier work[4] we decided to retain it.

However, in the *absence* of citric acid, chromium(III) was found *not* to reduce the amount of copper extracted. Citric acid certainly had a small effect on the extractability of copper by biquinolyl but when both chromium(III) and citric acid were present together there was a marked inhibitory effect which was scarcely alleviated by a 10-fold increase in the concentration of the extracting ligand. Typical results are shown in Table II.

The effect of a range of other tervalent ions on the extraction of $8 \times 10^{-5}M$ copper(II) from a solution containing citric acid ($0{\cdot}5M$) and hydroxylamine hydrochloride (3%) at pH $6{\cdot}0 \pm 0{\cdot}1$ by a $2 \times 10^{-3}M$ solution of biquinolyl in isoamyl alchohol was then examined. Figure 1 shows that iron(III) and lanthanum have practically no effect on the extraction of copper. The degree of extraction is progressively, but only slightly, reduced by aluminium; by contrast the effect of chromium(III) is almost dramatic.

TABLE II.—THE EFFECT OF CHROMIUM(III) AND CITRIC ACID ON THE EXTRACTABILITY OF COPPER BY BIQUINOLYL

[Chromium(III)], *M*	[Citric acid], *M*	[biquinolyl], $10^{-4}M$	Absorbance at 546 mμ
0	0	2·76	0·550
0·051	0	2·76	0·552
0	0·051	2·76	0·493
0·010	0·042	2·76	0·450
0·010	0·042	20·0	0·449

Each solution contained $9{\cdot}97 \times 10^{-7}$ mole of copper(II). Equilibrations were carried out as described in the experimental section, after adjustment of the aqueous phase to pH 6·1.

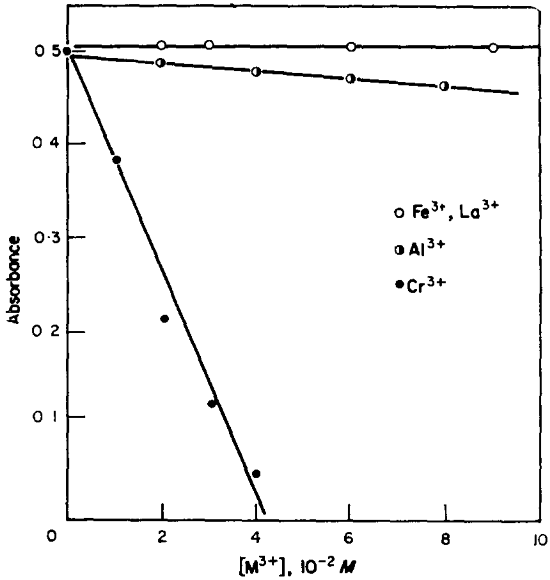


FIG. 1.—The effect on the extraction of copper (as measured from the absorbance of the complex $Cu(bq)_2^+$ extracted into isoamyl alcohol) of adding various tervalent cations.

To see whether the effect of iron(II) in counteracting the adverse effect of chromium(III) was unique to this metal, a series of extractions was carried out in which increasing amounts of zinc (or cobalt) were added to an aqueous phase containing $8 \times 10^{-5}M$ copper(II), 0·03*M* chromium(III), 0·5*M* citric acid and hydroxylamine hydrochloride at pH 6·1 ± 0·1. The results (Fig. 2) show very clearly the increase in the fraction of copper extracted even when the ratio $[M^{2+}]$:[citrate] = 1:50. When the relative concentration of zinc was increased 10-fold the fraction of copper extracted was restored to the value found when chromium(III) was absent and only citrate was incorporated into the aqueous phase.

These results are highly significant. Elwell's observation that iron(II) can effectively counteract the adverse effect of chromium(III) cannot now be related to its reducing powers—either in reducing chromium(III) to chromium(II) (which Elwell showed to be ineffective as an inhibitor),[2] or in reducing copper(II) to copper(I), or even as a "holding reductant"—for since iron(II) can be replaced by zinc(II) none of these hypotheses is tenable. Nor does it seem likely that the enhancement of extraction by iron(II), zinc(II) or cobalt(II) can simply be a matter of removing citrate from a complex containing copper alone since the citrate is present in such large excess. Indeed these results suggest that the inhibiting effect of chromium(III) must be due to its participation together with copper(II) and citrate ions in some form of ternary complex, and that the effect of the ions iron(II), zinc(II) and cobalt(II) is simply to displace copper(II) from this complex and thus free it for reduction and extraction.

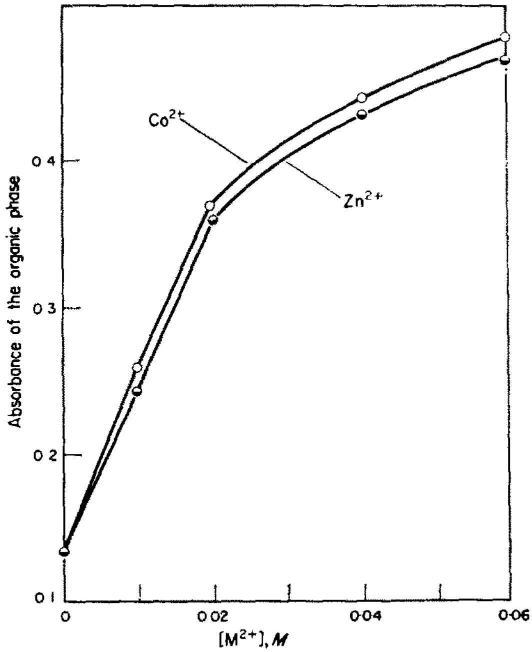


Fig. 2.—The effect of Co(II) and Zn(II) in increasing the amount of copper that can be extracted from a solution containing 8 × 10^{-6}*M* Cu(II), 0·03*M* Cr(III), 0·5*M* citric acid and hydroxylamine hydrochloride at pH 6·1.

Since cobalt(II) appeared to be even more effective than zinc(II) we examined the effect of other bivalent transition metal ions. The results of these experiments (Table III) showed that M^{2+} ions promote the extraction in the order

$$Mn^{2+} < Co^{2+} < Ni^{2+} < Fe^{2+} > Zn^{2+}$$

which, apart from the position of iron, happens to be identical with the Irving-Williams order of stabilities.[5,6] On prolonging the equilibration for 2–3 days the extraction of copper could be made quantitative in every case save with iron, showing that slow reaction rates form a feature of the reaction mechanisms that must also be taken into consideration. The anomalous behaviour of the iron was doubtless due to its slow oxidation to the ferric state as evinced (*inter alia*) by the gradual formation of a yellow citrato-complex in the aqueous phase; the concomitant decrease in hydroxylamine concentration will reduce the amount of copper(I) formed and extracted.

At this stage it appeared possible that the various phenomena could be explained in terms of a kinetically inert chromium(III)–copper(II)–citrate complex from which copper is (slowly) released on equilibration with a bivalent transition metal ion. However, when the method of continuous variations was applied to this system by examining the absorption spectra of an isomolar series of mixtures of copper citrate and chromium(III) citrate (each solution containing $1\cdot6 \times 10^{-2}M$ total metal and $6\cdot4 \times 10^{-2}M$ citric acid at pH 5·1) no evidence whatsoever was obtained for any interaction, for the absorption spectra of mixtures (not reproduced) proved to be exactly the sum of that of the two components and there was a very well-defined isosbestic point at 610 mμ. These results, however, merely exemplify the well-known kinetic inertness that characterizes reactions of chromium(III); indeed if the solutions were warmed to 80° and the spectra remeasured after the solutions had cooled to room temperature there was now clear evidence of interaction and the isosbestic point had disappeared (Fig. 3). No new clearly defined absorption bands appear, but if the results of the measurements on the heated solutions are expressed as a Job plot (Fig. 4) the distinct maxima at mole fraction $x = 0\cdot5$ demonstrates the formation of a ternary complex containing equal numbers of copper and chromium atoms. The formation of a ternary complex was confirmed by diluting members of the isomolar series 4-fold. Aliquot portions (1 ml) were mixed with 5% hydroxylamine hydrochloride (9 ml) and after adjustment to pH $5\cdot2 \pm 0\cdot1$ the aqueous mixtures were extracted with a $2 \times 10^{-3}M$ solution of 2,2′-biquinolyl in isoamyl alcohol (10 ml). The absorbance of each of the extracts was measured at 545 mμ in 0·5-cm cells, with the results shown in Fig. 5. The effect of the chromium is indicated by the reduction in absorbance below that based solely on the amount of copper present (broken line in Fig. 5). If the decreases in absorbance are plotted (right-hand scale) against the ratio [Cr]/([Cr] + [Cu]) the broad maximum value points to the existence of a

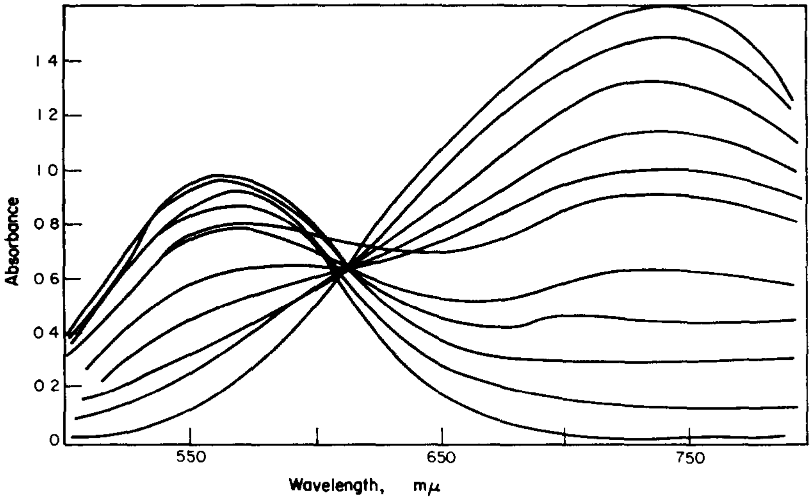


Fig. 3.—Absorption spectra for mixtures of x ml of $1\cdot6 \times 10^{-2}M$ Cu(II) in $6\cdot4 \times 10^{-2}M$ citric acid at pH 5·1 with $(10-x)$ ml of $1\cdot6 \times 10^{-2}M$ Cr(III) in $6\cdot4 \times 10^{-2}M$ citric acid at pH 5·1, which had been heated to 80° for a time and then cooled to room temperature before measurement.

The eleven curves of monotonically increasing absorbance at 750 mμ correspond to isomolar mixtures with $x = 0, 1, 2 \ldots 10$ respectively.

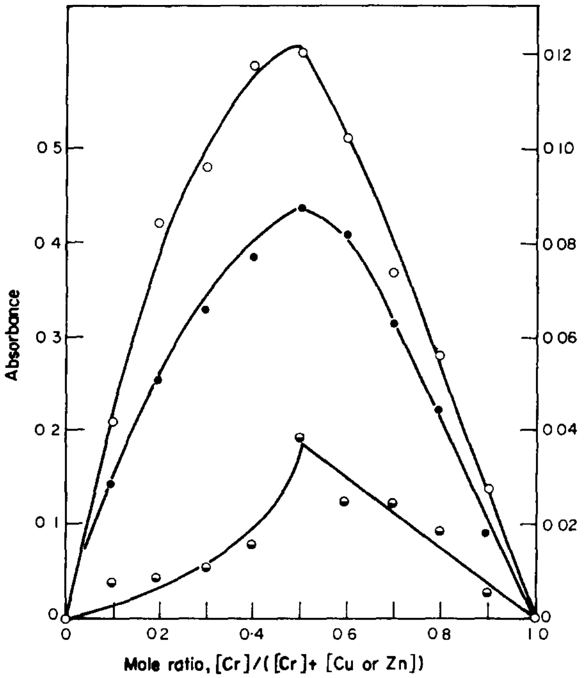


FIG. 4.—Job plot for ternary copper or zinc complexes.

○ —zinc at 557 mμ (right-hand scale); citric acid 0·12M, ([Zn] + [Cr]) = 0·04M

● —copper at 566 mμ} left-hand scale; citric acid

◒ —copper at 740 mμ} 0·064M; ([Cu] + [Cr]) = 0·016M.

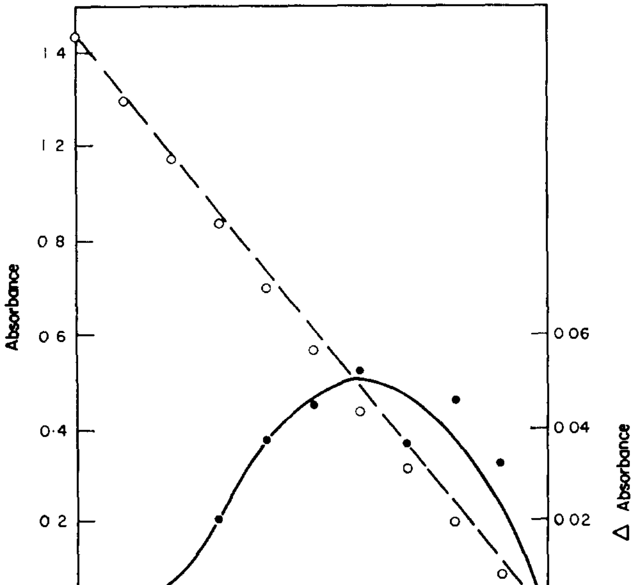


FIG. 5.—Job plot for extracted copper species.

○ —Absorbance of copper complex alone (left-hand scale)

● —Reduction in absorbance, caused by chromium (right-hand scale) ternary complex but does not clearly define the composition within the range [Cu]:[Cr] = 1:1 and 1:2.

That zinc will also form a ternary complex with chromium(III) and citrate ions was likewise established by the method of continuous variations using isomolar series with ([Zn] + [Cr]) = 0·04*M* and [citrate] = 0·12*M* at pH 5·6. Measurements were made at 557 mμ on solutions that had been heated at 80° for 1 hr and then cooled to room temperature. The results (Fig. 4; open circles) clearly establish the ratio [Cr(III)]:[Zn(II)] = 1:1 in this complex. When, however, the concentration of citrate was increased more than 3-fold so that the ratio [total metal]:[citrate] = 1:12·5 little positive evidence of a ternary complex could be detected. This somewhat surprising result is readily explicable if the ternary complex contains fewer citrate groups than the citrato-complexes of the individual members. Assuming that only two atoms of metal are involved, and omitting charges, we may write

$$\mathrm{Cr(III)(citrate)}_l + \mathrm{Zn(citrate)}_m \rightleftharpoons \mathrm{Cr(III)Zn(II)(citrate)}_n + (l + m - n)\mathrm{citrate} \qquad (1)$$

When copper enters the ternary copper–chromium–citrate complex there is a gradual shift in absorption to shorter wavelengths. The same effect is shown with zinc; but since this ion does not itself absorb in the visible region, changes in the absorption spectra are easier to follow. With increasing content of zinc the band due to the chromium shows an increase in intensity and there is a concomitant shift to shorter wavelengths as shown in Table V.

TABLE V.—THE EFFECT OF Zn(II) ON THE ABSORPTION SPECTRUM OF 0·03*M* CHROMIUM(III) IN 0·5*M* CITRIC ACID AT pH 6·0.

[Zinc], *M*	0	0·10	0·02	0·04	0·06	0·08
Absorbance*	0·80	0·84	0·85	0·88	0·94	1·01
λ_{max}; mμ	564	562	561	560	556	554

* All solutions were warmed to 80°C for 1 hr, cooled, and the pH readjusted to 6·0 before measurement in 1-cm cells. There was an isosbestic point at 469 mμ.

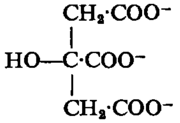
Since the citrate was present in such large excess these results cannot arise from the reduction in the number of citrate ions available for complexing chromium(III) as increasing amounts of zinc ions are added, for the addition of citrate to chromium(III) [or to copper(II)] causes a definite shift in the position of the broad absorption bands towards lower wavelengths, the shift being much more pronounced for copper than for chromium.

In order to confirm the formation of the postulated ternary complex by a technique independent of spectrophotometry the effect of adding increasing amounts of chromium(III) to a solution of copper(II) in a citrate medium was examined polarographically. The limiting diffusion current was found to decrease and the half-wave potential moved to a more negative value, both changes being indicative of the copper being bound in a stronger complex. The forms of the polarograms for copper in the presence of chromium and citrate are typical of those involving a slow decomposition of the complex at the cathode.[7,8] When increasing concentrations of zinc were added to solutions containing $4 \times 10^{-3}M$ copper(II), $6 \times 10^{-2}M$ chromium(III) and 0·4*M* citrate at pH 5·6 and the mixtures were heated at 80° for 1 hr, the polarograms of the (cold) solutions showed a gradual increase in the diffusion current of the copper so long as [Zn] $\leq$ [Cr], while $E_{\frac{1}{2}}$ appear to be unchanged. With further increase in the concentration of zinc the trend was reversed. No unambiguous interpretation of these results can be given, for the ionic strength varied from 1·7 to ~2·0. Since it is known that a change in ionic strength from 0 to 1 can shift the half-wave potential of a bivalent ion by ~15 mV to more negative values we cannot be sure that slight shifts in $E_{\frac{1}{2}}$ for copper to more positive values are not being compensated by ionic strength effects. Since all the processes show signs of being kinetically controlled we did not pursue these experiments.

DISCUSSION

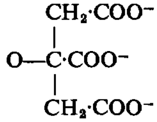
Although binuclear complexes of metals with certain hydroxy-acids (citric, tartaric and malic) are well known[10-14] there is still much controversy as to whether in the case of citric acid (H_4L) the ion(I) is involved or whether the central hydroxy group is able to lose a proton [as in (II)] and co-ordinate through the resulting negatively charged oxygen atom. It has been suggested that the binuclear vanadyl complex[14] does not involve an ionized hydroxy group because the O-H stretching frequency could still be detected in the mono-complex isolated as a solid at low pH. Other evidence against the participation of species (II) comes from rather old work[15] but other reports[12,16-18] favour this. Recent studies on complexes of copper with citric, malic and tartaric acids[12] show that binuclear complexes are formed in every case and that the *undissociated* hydroxy group is involved in the bonding. With the binuclear copper-citrate complex a further dissociation occurs.

(I; HL^{3-})



$$\begin{array}{c} CH_2\cdot COO^- \\ | \\ HO{-}C\cdot COO^- \\ | \\ CH_2\cdot COO^- \end{array}$$

(II; L^{4-})

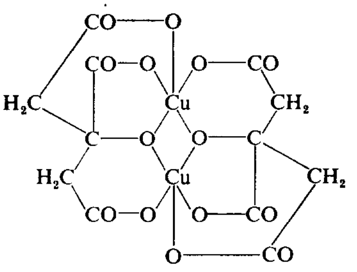


$$\begin{array}{c} CH_2\cdot COO^- \\ | \\ O{-}C\cdot COO^- \\ | \\ CH_2\cdot COO^- \end{array}$$

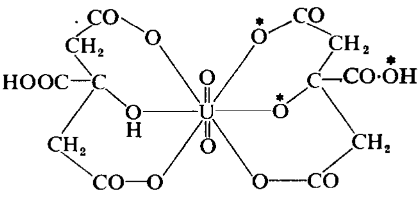
$$Cu_2(HL)_2^{2-} \rightleftharpoons Cu_2L_2^{4-} + 2H^+ (K = 10^{-8\cdot 1})$$

to give species formulated as (III).

A study of solutions containing uranyl(VI), aluminium(III) and citrate[8] has demonstrated the existence of a ternary complex involving one uranyl, one aluminium and two citrate residues per molecule. The spectral and polarographic behaviour of the uranyl complex would best be interpreted by postulating that one hydroxy group had lost a proton and that the hydroxylic oxygen participated in the bonding as in (IV). Co-ordination to aluminium is then assumed to involve the three oxygen atoms marked with an asterisk. This must affect the spectra (as found experimentally) to



(III)



(IV) The two uranyl oxygen atoms lie above and below the plane of the paper.

an extent which would not occur if the two metals were isolated even by a $-CH_2-$ group. Similar spectral changes occur on forming the ternary complexes described in this paper.

If a molecular model is constructed involving 6-co-ordinate chromium(III) and two citrate ions co-ordinated through the hydroxy oxygen atoms, two carboxylate ions remain free and the resulting complex may be formulated as CrL_2^{5-}, $CrL(HL)^{4-}$, or $Cr(HL)_2^{3-}$ depending on how many of the hydroxy protons are dissociated. Such a complex behaves as a quadridentate ligand, for its conformation is such that the two free carboxyl groups will readily co-ordinate to a second cation in the *cis*-position of a square-planar or octahedral co-ordination sphere and a convenient "hole" is presented in which the ion can fit with the corresponding *trans*positions occupied by the two hydroxy oxygen atoms of the citrate residues. This is illustrated in Fig. 6 which represents a scale Dreiding model; the hydroxy protons have been deliberately omitted. In a less symmetrical arrangement (Fig. 7) the two citrate ions are again co-ordinated in a strain-free manner to give one free carboxylate ion, $-COO^-$, and one free acetate ion, $-CH_2 \cdot COO^-$. These will co-ordinate to a second ion most favourably in the *trans*-position, and one of the *cis*-positions is in precisely the correct location for co-ordination to one of the hydroxy oxygen atoms; the remaining co-ordination site(s) could clearly be occupied by water molecules without steric hindrance. It is not clear whether such a completely strainless 3-point attachment would be more probable than the 4-point attachment shown in Fig. 6 where some distortion from a regular square-planar (or octahedral) arrangement would seem inevitable, but this latter arrangement would be favoured by entropy considerations.

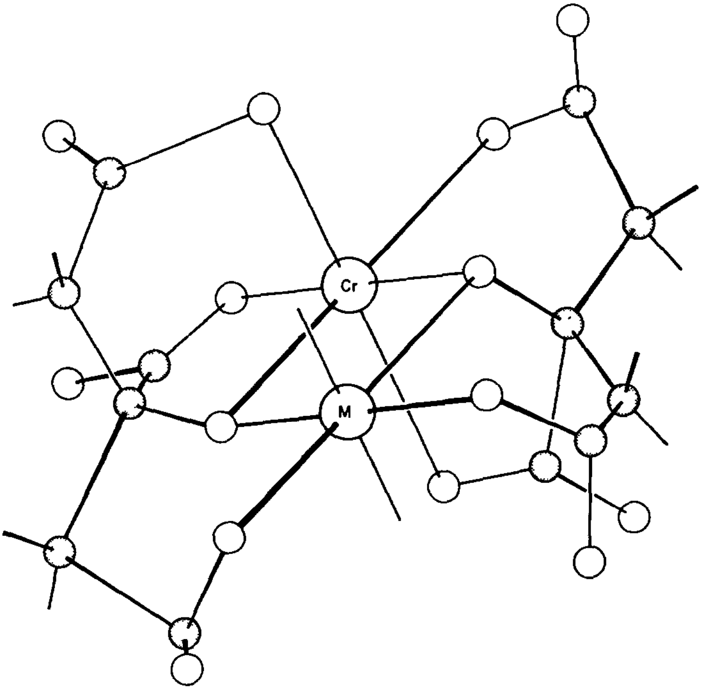


FIG. 6

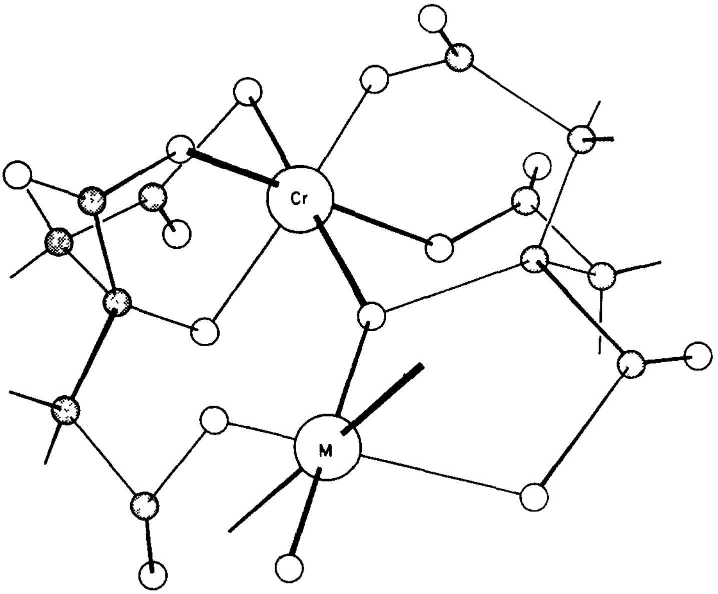


Fig. 7

It is noteworthy that the ternary complex is formed in solutions containing far more than enough citrate to complex separately all the metals present. This can only mean that the stability of the ternary complex is greater than those of the citrato-complexes of the individual metals. The high stability of the ternary uranyl–aluminium–citrate was explained by the reduction in the negative charge on the uranyl–citrate complex caused by incorporating an aluminium cation. The same considerations will obviously apply in the present chromium–citrate–transition metal complexes and the entropy increase illustrated in equation (1) will be a further stabilizing factor if $l = n = 2$ since m must be >1.

At this stage it is important to comment on what might appear to be a discrepancy between the slow rate of formation at room temperature of the copper–chromium–citrate complex (as demonstrated during studies of its composition by the method of continuous variations, *vide supra*) and the normal conditions for the determination of copper by biquinolyl. It would appear that chromium(III) ought not to interfere seriously and indeed this is found to be the case if, as in these experiments, the excess of citrate is no greater than 4-fold, and if the solutions are not allowed to get hot. When the concentration of chromium greatly exceeds that of the copper and that of the citrate is greater still, the rate of (ternary) complex-formation will be increased; an additional factor is the rise in temperature when the citric acid (present as such in the original solution) is neutralized.

It is worth noting that in Elwell's final procedure,[2] copper is reduced to the cuprous state and excess of sulphur dioxide is boiled off before addition of 50% citric acid solution and neutralization. At this stage chromium(III) will certainly be masked as the kinetically inert citrato-complex. Iron(II) present (in excess of the amount of copper) from alloy steels, or added deliberately to other sample solutions [ref. 2, p. 513, Note (2)] will then serve two functions. It will form the ternary complex chromium(III)–iron(II)–(citrate)$_2$ from which any copper(II) would be excluded by a mass-action effect, and it would also serve as a holding reductant to inhibit the re-oxidation of copper(I) during the brief period before its extraction as its biquinolyl complex.

In conclusion it should be pointed out that the formation of unsuspected ternary compounds may explain a number of anomalous observations and unexplained interferences in analytical procedures. Thus Flaschka[20] observed an unexpected reduction in reaction rate when copper was titrated at pH 8 with triethylenetetramine in a tartrate solution that also contained aluminium. Investigation showed that a kinetically inert tartrate-complex containing both copper and aluminium in the molar ratio 1:2 had been formed. It seems likely that further examples of binuclear (or polynuclear) complexes containing more than one metallic element remain to be discovered and that some at least will prove of significance analytically.

EXPERIMENTAL

Reagents

Reagents of analytical grade were used throughout.

Copper(II) solutions. Prepared from known weights of pure $CuSO_4\cdot 5H_2O$ in demineralized water.

Isoamyl alcohol. Redistilled just before use, the fraction boiling at 130°C being used.

Absorption spectra were measured with a Unicam SP500 spectrophotometer or recorded on the SP700 or SP800 instruments. Hydrogen-ion concentrations were controlled and measured with a Radiometer pH-meter and a Radiometer Polariter PO3 was used in the polarographic studies.

Procedure

The effect of components in the aqueous phase on the extraction of copper into isoamyl alcohol containing 2,2′-biquinolyl was studied by the following procedure. An aliquot of a stock aqueous solution of copper(II) was placed in a beaker together with known amounts of any other substances. The pH was adjusted to the desired value with sodium hydroxide and hydrochloric acid and the mixture heated at 80° for 1 hr, and then allowed to cool. The pH was readjusted to its original value and the solution transferred to a volumetric flask. Hydroxylamine hydrochloride solution (5%), previously adjusted to the same pH, was then added and the whole made up to the mark.

An aliquot of this solution (10·0 ml) was placed in a glass-stoppered (40 ml) centrifuge tube and an equal volume of isoamyl alcohol (10 ml) containing a known concentration of biquinolyl was added. The tubes were shaken mechanically for 30 min at room temperature and then the contents were centrifuged and an aliquot of the organic phase was transferred to a spectrophotometer cell. The absorbance was measured at 546 mμ against a blank of isoamyl alcohol and the concentration of copper was calculated from previously determined calibration curves.

The effect of 0·04M transition metal ion solutions (Mn(II), Fe(II), Co(II), Ni(II) or Zn(II)) on the extraction of $8 \times 10^{-5}M$ copper from a solution containing 0·5M citric acid, 0·03M chromium(III) and hydroxylamine (5%) by $2 \times 10^{-3}M$ biquinolyl dissolved in isoamyl alcohol gave the results shown in Table III, row (*a*). After these measurements (1-cm cells) the solutions were returned to their respective centrifuge tubes and the shaking was continued for 2½ days; the results are shown in Table III row (*b*).

TABLE III.—EXTRACTION OF COPPER FROM CITRATE BUFFER AT pH 5·2 CONTAINING BIVALENT TRANSITION METAL IONS AS WELL AS CHROMIUM(III)

Cation added		None	Mn(II)	Co(II)	Ni(II)	Fe(II)	Zn(II)
Absorbance	(*a*)	0·131	0·238	0·243	0·262	0·294	0·229
at 546 mμ	(*b*)	0·501	0·501	0·501	0·501	0·301	0·501

Solutions of $1{\cdot}6 \times 10^{-2}M$ copper(II) [or chromium(III)] nitrate with a 4-fold excess of citric acid were prepared and adjusted to pH 5·1 ± 0·1. Isomolar mixtures were prepared and their spectra recorded with a Unicam SP700. Absorbances at 740 and 566 mμ were measured (*a*) immediately after mixing and (*b*) after each mixture had been heated for a few hours at 80° and cooled again to room temperature. The results are given in Table IV.

TABLE IV.—METHOD OF CONTINUOUS VARIATION APPLIED TO ISOMOLAR MIXTURES OF COPPER(II) CITRATE AND CHROMIUM(III) CITRATE

[Cu(II)], *M*	[Cr(III)], *M*	Absorbance at 740 mμ (*a*)	Absorbance at 740 mμ (*b*)	Absorbance at 566 mμ (*a*)	Absorbance at 566 mμ (*b*)
0·0160	—	1·56	1·56	0·22	0·22
0·0144	0·0016	1·42	1·46	0·30	0·33
0·0128	0·0032	1·27	1·29	0·38	0·41
0·0112	0·0048	1·10	1·12	0·46	0·50
0·0096	0·0064	0·95	0·98	0·55	0·60
0·0080	0·0080	0·79	0·89	0·64	0·79
0·0064	0·0096	0·63	0·63	0·72	0·80
0·0048	0·0112	0·46	0·47	0·80	0·87
0·0032	0·0128	0·32	0·30	0·88	0·92
0·0016	0·0144	0·18	0·14	0·95	0·96
—	0·0160	0·02	0·02	0·97	0·97

Zusammenfassung—Bei der Bestimmung kleiner Kupfermengen in gewissen Legierungen durch Solventextraktion des Bis-Chelats von Kupfer(I) mit 2,2'-Bichinolyl sollen die Kupferwerte in Gegenwart von Chrom(III) zu niedrig sein. Die Störung durch Chrom(III) kann durch Zugabe von Eisen(II) beseitigt werden. Es wird jetzt gezeigt, daß die Störung durch Chrom auf Bildung eines kinetisch stabilen ternären Komplexes aus Chrom(III), Kupfer(II) und Citrationen beruht, der von beiden Metallen die gleiche Atomanzahl enthält. Aus diesem Komplex kann Kupfer durch irgendeines der Übergangsmetalle Mn(II), Fe(II), Co(II), Ni(II) und Zn(II) verdrängt werden. Es wird gezeigt, daß Zink einen ternären Komplex bildet, der dem vom Kupfer formal analog ist. Die Bildung der ternären Komplexe wurde polarographisch untersucht. Es wird ein Überblick über die Bildung binuklearer Komplexe verschiedener Hydroxysäuren gegeben und eine wahrscheinliche Struktur für den ternären Komplex vorgeschlagen, die seine Stabilität und seine kinetische Trägheit erklärt. Es werden Analogieschlüsse gezogen zwischen diesem Komplex und ternären Komplexen von UO_2(VI)–Al(III)–Citrat und Cu(II)–Al(III)–Tartrat, die ebenfalls Störungen in erprobten analytischen Vorschriften verursachen.

Résumé—Dans le dosage de petites quantités de cuivre dans certains alliages par extraction en phase liquide du bis-chélate du cuivre(I) avec le 2,2'-biquinolyle, on a rapporté que la récupération du cuivre est faible lorsque le chrome(III) est présent. L'influence défavorable du chrome(III) pouvait être surmontée par addition de fer(II). On montre maintenant que l'influence inhibitrice du chrome est attribuable à la formation d'un complexe ternaire cinétiquement inerte des chrome(III), curvie(II) et ions citrate contenant un nombre égal d'atomes de chacun des deux métaux. On peut déplacer le cuivre de ce complexe par n'importe lequel des cations de transition Mn(II), Fe(II), Co(II), Ni(II) et Zn(II). On a montré que le zinc forme un complexe ternaire analogue par sa formule à celui du cuivre. On a étudié polarographiquement la formation des complexes ternaires. On a passé en revue la formation de complexes binucléaires de divers hydroxyacides et propose une structure probable pour le complexe ternaire, qui explique sa stabilité et son inertie cinétique. On dégage des analogies entre ce complexe et des complexes ternaires de UO_2(VI)—Al(III)—citrate et Cu(II)—Al(III)—tartrate qui causent également des interférences dans des techniques analytiques établies.

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SOLUBILITY OF WATER IN HYDROCARBONS AS A FUNCTION OF WATER ACTIVITY*

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Summary—A method is described for determination of low solubilities of water in organic liquids (such as are used in solvent extraction) by vacuum distillation of a suitably sized equilibrated sample through magnesium perchlorate in a conventional weighing tube. Tritium tracer is used to estimate completeness of water absorption. At the same time, the results serve to evaluate the ratio of tritium and water distribution coefficients for use in collateral determinations of water solubility by simple liquid–liquid distribution. The solubility of water in benzene, n-hexane, and cyclohexane is 0·0363, 0·00362, and 0·00345*M* respectively. The dissolved water follows Henry's law, the mole fraction constants being 0·00323, 0·000476 and 0·000375 respectively.

IN STUDIES of solvent extraction systems we have a recurring need for information on the water contents of various water-immiscible organic diluents, in equilibrium not only with pure water but also with solutions over a range of water activities. From our own experience and the variations among published results, Karl Fischer titration is not very satisfactory for these low-level analyses. Use of tritium as an analytical tracer[1] is simple, precise and sensitive, but (in contrast to tracer isotopes of heavier elements) the isotope effect between T and H cannot be ignored. Moule has discussed the fractionation factors of H_2O, HDO and HTO between water and benzene, and has reported a sophisticated isotope-dilution method for measuring the solubility of water in non-polar organic liquids.[2] We have developed a relatively simple method for measuring water solubility, based on use of tritium tracer (1) to monitor the recovery of water in a conventional gravimetric water determination, and (2) to measure tritium distribution between aqueous and organic phases over a range of water activities. Besides giving a direct measurement of water content at one point, the first step provides the ratio of water and tritium distribution coefficients needed to calculate water distributions from the tritium distributions of the second step.

EXPERIMENTAL

Reagents

Tritiated water. Tritiated water at 5 C/ml, New England Nuclear Corp., was diluted to about 1 mC/ml for use. Tritium activity in initial and product samples was determined by liquid scintillation counting with a Packard Tri-Carb Scintillation Spectrometer. Counting efficiency was checked by use of tritiated biphenyl as an internal standard.

Solvents. Phillips Petroleum Corp. 99% n-hexane was further purified by shaking it with concentrated sulphuric acid until no further discoloration occurred. It was then washed with water and dried with sodium sulphate. Benzene was the usual thiophene-free reagent, recrystallized three times. Cyclohexane was spectral-grade reagent.

Salts. Salts used to set the water activities,[3,4] listed in Table I, were analytical-grade reagents. To avoid possible water contamination and resulting error in hydrogen: tritium ratios, lithium chloride

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* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

was used only from freshly-opened bottles. Sodium bromide and the hydrates $MgCl_2.6H_2O$ and $K_2CO_3.1{\cdot}5\,H_2O$ were dried over magnesium perchlorate. The hydrated salts were also handled, in parallel tests, by total dissolution in warm solution to permit isotopic equilibration. Enough salt reprecipitated at 25° to ensure continued saturation, and the nominal water of hydration was included in calculation of the hydrogen:tritium ratio. Chloride and carbonate analyses of the resulting solutions confirmed that both methods gave correct results. The magnesium perchlorate used was reagent grade.

TABLE I.—WATER ACTIVITIES IN SATURATED SALT SOLUTIONS (MOLE FRACTION SCALE)*

$K_2Cr_2O_7$	0·980	KBr	0·807	$K_2CO_3.1{\cdot}5\,H_2O$	0·428
KNO_3	0·925	NaCl	0·753	$MgCl_2.6\,H_2O$	0·330
KCl	0·843	NaBr	0·577	LiCl	0·110

* From Ref. 3. LiCl also used in unsaturated solutions, water activities from Ref. 4.

Distribution measurements

The aqueous phases consisted of tritiated water, either pure or containing a salt to adjust the water activity to a desired level. Usually the salt (Table I) was used at saturation, with excess of solid present, to give an invariant system. Unsaturated lithium chloride solution was used in a few tests, its concentration after equilibration being determined by Mohr chloride titration. In each test a small amount of the chosen aqueous phase was shaken with 10 ml of the organic liquid in a small screw-capped vial on a wrist-action shaker at 25°. After at least 1 hr, the phases were allowed to separate and then were sampled for tritium analysis. In some cases the phases were separated by centrifugation; these showed no detectable change in tritium content.

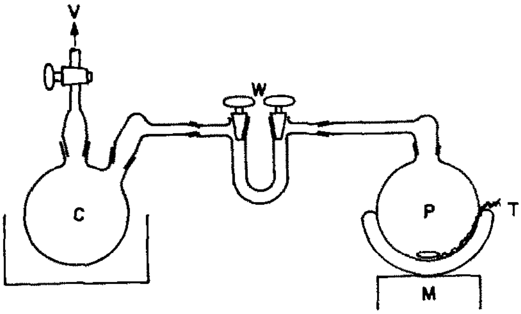

FIG. 1.—Distillation system for gravimetric water determination.

P: Distillation pot (500 or 1000 ml) in heating mantle with magnetic stirrer *M* and thermocouple *T*. *W*: Absorption tube charged with magnesium perchlorate. *C*: Receiver, cooled with ice or dry-ice. *V*: Vacuum system.

Gravimetric measurements

A volume of the organic liquid (100–600 ml) sufficient to dissolve a convenient weight of water was equilibrated with a slight excess of tritiated water in a separatory-funnel, by intermittent shaking over a period of at least 8 hr in a thermostat. The phases were allowed to separate for at least 16 hr, and then were sampled for tritium analysis. Most of the organic phase was weighed (± 0·1 g) into a boiling flask, which was made the pot of a closed distillation system (*P* of Fig. 1). After the distillation train had been carefully evacuated and closed off from the vacuum system, the organic sample was distilled through the magnesium perchlorate weighing tube (*W*) into the cold receiving flask (*C*). The pot temperature was held not much above room temperature, usually below 40°.

The weighing tube was evacuated again to remove any condensed or sorbed trace of the organic compound. It was then opened briefly to atmospheric pressure and weighed, with the technique described by Trusell.[5] The magnesium perchlorate was then dissolved for measurement of its tritium content. The pot was rinsed with 5 ml of acetone, which was counted to measure any residual water. A sample of the organic condensate was also counted to measure any water that had escaped absorption in the weighing tube. The total tritium found was checked against the tritium concentration found initially in the organic phase.

In most of the tests, the distillation system up to the cold receiver was enclosed in a light plastic bag that was loosely inflated with a slow stream of dried air (Drierite and dry-ice cold trap), so that a completely leak-free distillation system was not needed. Although not essential, this proved to be a worthwhile convenience.

RESULTS AND DISCUSSION

The gravimetric results for water solubilities in three frequently used diluents are presented in Table II, along with other values from the recent literature. The solubility in benzene agrees well with Moule's value, whereas most of the other values for benzene range somewhat lower. (We interpolated to 25° from Englin's results listed at 10° intervals, and interpolation error might contribute to the difference; however, a plot of Englin's values for benzene falls below Moule's by 10% at 25° and by 28% at 50°. Moule's value, reported for 24·54°, was also adjusted to 25°. The other values cited were reported for 25°.) The solubilities found by us are considerably lower than Englin's for n-hexane and cyclohexane, and higher than Johnson's for cyclohexane.

TABLE II.—MOLAR SOLUBILITY OF WATER IN ORGANIC DILUENTS AT 25°C

Source and method	Benzene	n-Hexane	Cyclohexane
This work: tritium-monitored gravimetric	0·0363	0·00362	0·00345
Moule,[5] isotope dilution	0·0359		
Masterton,[6] K. Fischer titrn.	0·0347		
Johnson,[7] K. Fischer titrn.	0·0349		0·0024
Högfeldt,[8] K. Fischer titrn.	0·032		
Englin,[9] CaH_2 method	0·032*	0·0043*	0·0069*
Others†	0·006– 0·036	0·0038	0·002– 0·008

* Our interpolation from solubilities reported at 10° intervals between 0 and 50°C.

† Range of values reported in several other publications since 1954.

In all of our tests, the tritium tracer showed that less than 0·1% of the water either remained in the distillation pot or passed through the absorber to the receiver; the loss was less than 0·05% in the case of benzene. These are negligible quantities. However, if larger losses should occur, they can be corrected for by means of the tritium distribution. Such correction will not require any allowance for the difference in vapour pressures between normal and tritiated water, for so long as nearly all of the water is collected, there will be almost no *net* fractionation.

The ratio of water and tritium distribution coefficients, $D_{(H_2O)}/D_{(T)}$, is given by

$$\frac{(\text{mg H}_2\text{O/g})_{\text{org}}}{(\text{mg H}_2\text{O/g})_{\text{aq}}}\Big/\frac{(\text{T cpm/g})_{\text{org}}}{(\text{T cpm/g})_{\text{aq}}} = \left(\frac{\text{mg H}_2\text{O}}{\text{T cpm}}\right)_{\text{org}} \times \left(\frac{\text{T cpm}}{\text{mg H}_2\text{O}}\right)_{\text{aq}}.$$

The aqueous ratio $(\text{T cpm/mg H}_2\text{O})_{\text{aq}}$ was determined by counting a sample of each equilibrium aqueous phase, and was checked by calculation from the initial aqueous phase count-rate and the quantities transferred to the organic phase. The organic-phase ratio $(\text{mg H}_2\text{O/T cpm})_{\text{org}}$ was determined directly from the weight of water and the tritium count-rate found in the absorption-weighing tube, and was checked by calculation from the gravimetric water solubility and the measured count-rate of a sample of the equilibrium organic phase. The resulting distribution coefficient ratios were 1·07 for benzene, 1·23 for n-hexane and 1·27 for cyclohexane. The value of the distribution coefficient ratio found for benzene is considerably smaller than the fractionation factor, 1·16, estimated by Moule.[2] At present we have no explanation to offer for this difference.

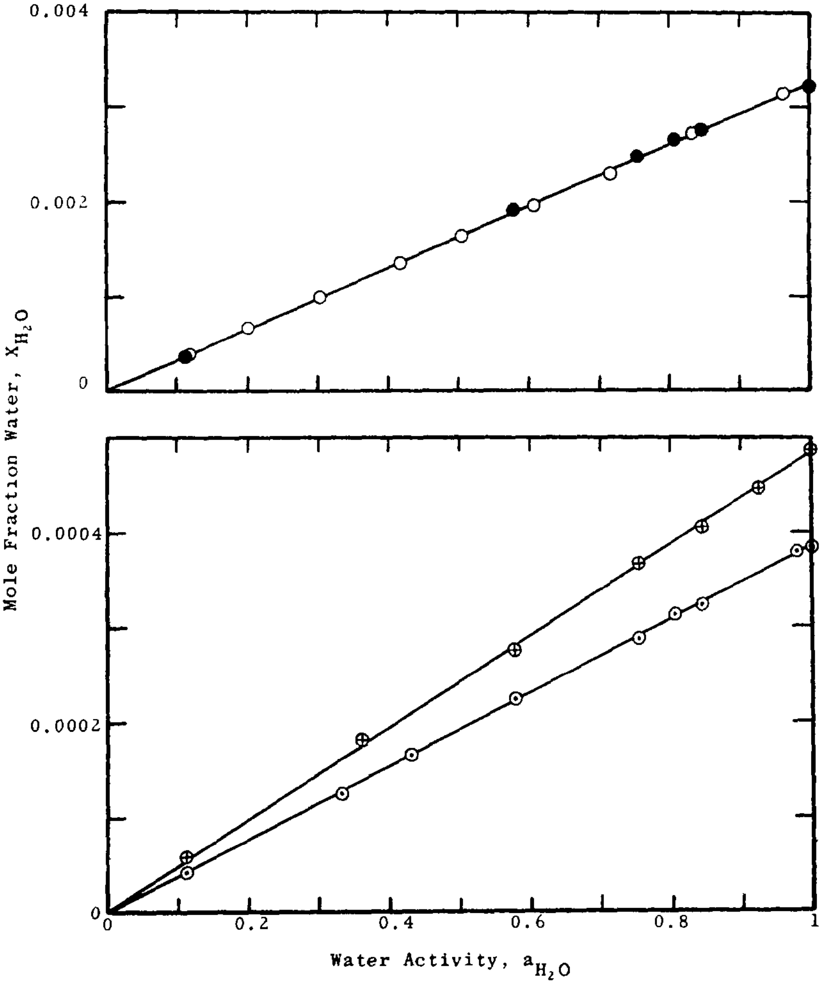

FIG. 2.—Water contents of organic diluents as a function of water activity (Henry's law plots).
⊙ Cyclohexane, ⊕ n-hexane, ● benzene (saturated salt solutions); ○ benzene (unsaturated LiCl solutions).

Liquid–liquid distribution of the tritium tracer between aqueous solutions and each of the three hydrocarbons was directly proportional to the water activity, a_{H_2O}, over the entire range. If it is correct that the ratio of tritium and water distribution coefficients remains essentially constant in each system, this means that water dissolved in benzene, n-hexane and cyclohexane follows Henry's law for all water activities (Fig. 2), the mole fraction constants being 0·00323, 0·000476 and 0·000375, respectively.

The (thermodynamic) activity of the tritiated species (presumably HTO) may not be exactly proportional to the activity of water throughout the series of salt solutions, and hence the ratio of distribution coefficients may not be constant. However, if the activity does vary to a significant extent, it would mean that water deviates from Henry's law in exactly the same way in all three diluents (and some others*), and also in just the right way to match and cancel the variation in ratio of distribution coefficients. We consider this highly improbable, and hence have not considered it necessary to check the water contents at intermediate water activities by the gravimetric method.

We estimate the precision of the gravimetric measurements to be better than 1%. Which steps limit the precision depends on choice of the volume for distillation, specific activity of the tritium, and size of sample taken for counting. At the lower solubilities the distillation volumes were kept small; so the precision depended on the reproducibility of absorption tube weight, *e.g.*, 25 mg net increase in 70 g gross weight (balanced against a tare tube), weighable to <0·01 mg and reproducible to <0·1 mg or <0·5%. Use of tritium at the 1 mC/ml level was sufficient to limit the uncertainty of water recovery to within 0·05% if 0·1-ml samples of the benzene distillate were counted and to within 0·1% with 1-ml samples of the other hydrocarbons. The counting statistics of the relatively large quantities of tritium in the aqueous phase, saturated organic phase, and dissolved magnesium perchlorate gave an error of <0·4%.

CONCLUSIONS

Low levels of water dissolved in moderately volatile hydrocarbons, *etc.*, can be determined relatively simply by gravimetric absorption monitored by tritium tracer, with no specialized equipment other than a suitable counter for the tritium. After being determined at one or a few water activities, water solubilities can be obtained at other activities even more simply by tritium-traced liquid–liquid distribution.

Water dissolved in benzene, n-hexane and cyclohexane follows Henry's law over the entire range of water activities. The solubilities at $a_{H_2O} = 1$ are respectively 0·0363, 0·00362 and 0·00345 M, corresponding to mole fractions of 0·00323, 0·000476 and 0·000375 (*i.e.*, Henry's law constants).

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* Distribution measurements for n-octane, toluene, and carbon tetrachloride, to be published later, also show tritium distribution directly proportional to the water activity.

Zusammenfassung—Eine Methode zur Bestimmung kleiner Löslichkeiten von Wasser in organischen Flüssigkeiten (wie sie bei der Solventextraktion verwendet werden) wird beschrieben, wobei eine equilibrierte Probe geeigneter Größe im Vakuum durch Magnesiumperchlorat in einem üblichen Wägeröhrchen destilliert wird. Zum Nachweis vollständiger Absorption des Wassers wird Tritium-Tracer verwendet. Gleichzeitig dienen die Ergebnisse zur Bestimmung des Verhältnisses der Verteilungskoeffizienten von Tritium und Wasser bei Parallelbestimmungen der Wasserlöslichkeit durch einfache flüssig-flüssig-Verteilung. Die Löslichkeit von Wasser in Benzol, n-Hexan und Cyclohexan ist 0,0363; 0,00362 bzw. 0,00345*M*. Das gelöste Wasser folgt dem Henryschen Gesetz, wobei die Molenbruchkonstanten 0,00323; 0,000476 bzw. 0,000375 betragen.

Résumé—On décrit une méthode de détermination de faibles solubilités de l'eau dans des liquides organiques (comme ceux utilisés dans l'extraction par solvant) par distillation sous vide d'un échantillon équilibré de dimensions convenables à travers du perchlorate de magnésium dans un tube à peser ordinaire. On utilise le tritium comme traceur pour estimer le caractère total de l'absorption de l'eau. En même temps, les résultats servent à évaluer le rapport des coefficients de partage du tritium et de l'eau pour l'utiliser dans des déterminations collatérales de solubilité de l'eau par simple partage liquide–liquide. La solubilité de l'eau dans le benzène, le *n*-hexane et le cyclohexane est 0,0363; 0,00362 et 0,00345*M* respectivement. L'eau dissoute suit la loi de Henry, les constantes de fraction de mole étant 0,00323; 0,000476 et 0,000375 respectivement.

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SOLVENT EXTRACTION BEHAVIOUR OF THIOCYANIC ACID

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Summary—The solvent extraction behaviour of thiocyanic acid with isobutyl methyl ketone and xylene as solvents is described. In the ketone system the thiocyanic acid is solvated in the organic phase to give a complex with a proposed composition of HSCN . 2IBMK. Deviations from ideal behaviour, which can be attributed to variations in the activity coefficient of the acid in the aqueous phase, are shown.

EXTRACTIONS of metal thiocyanate complexes from aqueous solutions into water-immiscible solvents have been extensively reported.[1–3] The thiocyanate/water-insoluble ketone systems in particular have aroused considerable interest in the separation and purification of hafnium and zirconium.[4–6] However, very little work has been done on the mechanisms involved in these extraction systems. It has been qualitatively shown that thiocyanic acid can be extracted from aqueous solutions with ether.[7] Investigations on the extraction behaviour of thiocyanic acid have also been conducted with TBP[8] and di-isopentylmethylphosphonate[9] as solvents. Vinarov *et al.*[10] studied the extraction of thiocyanic acid by acetophenone from a salted system.

Although there does not appear to be agreement in the literature on the exact strength of thiocyanic acid, it is generally accepted that it is a strong acid.[11–16] In this paper it is assumed that thiocyanic acid is almost completely ionized in aqueous solution under the experimental conditions used, but for the sake of brevity it will be indicated by HSCN.

Metal thiocyanates are normally extracted from highly salted solutions, but preliminary experiments indicated that it is extremely difficult to explain the extraction behaviour of thiocyanic acid in such solutions.

The purpose of this investigation was to gain a clearer insight into the fundamental processes involved in the liquid–liquid extraction behaviour of thiocyanic acid in unsalted solutions, using xylene as an example of a non-polar solvent, and isobutyl methyl ketone as an example of a polar solvent.

EXPERIMENTAL

Reagents

Isobutyl methyl ketone (IBMK). BDH "Laboratory Reagent" grade.

Sodium thiocyanate. Merck "Pure" grade. All other reagents were of analytical reagent grade.

Procedure

All the distribution experiments in this study were carried out by the batch-extraction method, at 25° ± 0·5°, with equal volumes (10 ml) of both phases. Intimate mixing of the phases was effected by stirring for 2 min with high-speed stirrers equipped with glass paddles. Clean separation of the phases was aided by centrifugation.

Thiocyanic acid (HSCN) solutions were prepared by mixing a solution of sodium thiocyanate with sulphuric, hydrochloric or perchloric acid and extracting with IBMK. The solution of thiocyanic acid in IBMK was then washed twice with small quantities of distilled water to remove any mechanically entrapped mineral acid, and centrifuged to remove any free water. Aqueous solutions of thiocyanic acid were prepared by back-extraction of the IBMK-thiocyanic acid solutions with distilled water.

When the distribution of thiocyanic acid between water and IBMK was determined, the HSCN was initially in the organic phase. With xylene as organic phase, aqueous HSCN solutions were used, twice prewashed with xylene to remove traces of dissolved IBMK.

After it had been determined that thiocyanate and hydrogen ions are extracted in equivalent amounts, equilibrium HSCN concentrations in both phases were determined only by direct titration with standard sodium hydroxide, Bromocresol Green being used as indicator. This agrees with the results of ether extractions reported by Lewis and Skoog.[17]

In experiments involving constant equilibrium thiocyanate concentrations in the aqueous phase, the aqueous thiocyanate concentrations were determined argentimetrically.[17]

Volume changes of the phases were determined by extracting aqueous HSCN solutions with IBMK in graduated cylinders with ground-glass stoppers, and reading the volume changes after the phases had completely separated. No significant volume changes were observed when xylene was used as solvent.

RESULTS AND DISCUSSION

In the extraction of HSCN by organic solvents, equilibrium is attained very rapidly. Thus, in a typical experiment with IBMK as solvent, and extraction times of 5 sec, 10 sec, 1, 5, 10 and 30 min, the distribution coefficient values were 0·786, 0·786, 0·785, 0·786, 0·764 and 0·784, respectively.

In order to ascertain that true equilibrium conditions were reached in the distribution of HSCN between IBMK and water, two series of experiments were performed; one with HSCN initially in the IBMK and the other with the HSCN initially in the aqueous phase. It was found that for a particular equilibrium acid concentration in the aqueous phase, the distribution coefficient was constant. Furthermore, it was shown that the distribution of HSCN is also independent of the mineral acid used in its preparation. These results were taken to be sufficient proof that the HSCN used in this study was not contaminated with any mineral acid.

IBMK system

Fairly large volume changes of the phases were observed during the extraction of HSCN with IBMK. The increase in volume of the IBMK phase, as a function of the HSCN concentration in this phase, is shown in Fig. 1.

When HSCN is extracted by IBMK, and if solvation of the extracted acid occurs in the organic phase, the reaction may be formulated as follows:

$$\mathrm{H^+_{aq}} + \mathrm{SCN^-_{aq}} + x\mathrm{IBMK_{org}} \rightleftarrows \mathrm{HSCN}\,.\,x\mathrm{IBMK_{org}} \tag{1}$$

with the following equilibrium constant:

$$K = \frac{[\mathrm{HSCN}\,.\,x\mathrm{IBMK}]_{\mathrm{org}}}{[\mathrm{H^+}]_{\mathrm{aq}}[\mathrm{SCN^-}]_{\mathrm{aq}}[\mathrm{IBMK}]^{x}_{\mathrm{org}}} = \frac{D_{\mathrm{HSCN}}}{[\mathrm{H^+}]_{\mathrm{aq}}[\mathrm{IBMK}]^{x}_{\mathrm{org}}} \tag{2}$$

where

$$D_{\mathrm{HSCN}} = \frac{[\mathrm{HSCN}]_{\mathrm{org}}}{[\mathrm{SCN^-}]_{\mathrm{aq}}}\,.$$

Thus

$$D_{\mathrm{HSCN}} = K[\mathrm{H^+}]_{\mathrm{aq}}[\mathrm{IBMK}]^{x}_{\mathrm{org}}$$

and

$$\log D_{\mathrm{HSCN}} = \log K + \log\,[\mathrm{H}^+]_{\mathrm{aq}} + x \log\,[\mathrm{IBMK}]_{\mathrm{org}} \tag{3}$$

where the brackets denote concentrations. For a stricter definition, concentrations should be replaced by activities, but, as these are unknown, concentrations were used as an approximation.

Now from equation (3), if the equilibrium acid concentration in the aqueous phase is kept constant, then a log–log plot of D_{HSCN} as a function of the equilibrium IBMK concentration should give a straight line with slope equal to the solvation number of the IBMK for the HSCN. The IBMK concentration was varied by dilution with n-heptane, which by itself gave negligible extraction of HSCN. The resulting plot was a straight line (Fig. 2) with a slope of 2 indicating that the solvate formed [equation (1)] is HSCN . 2IBMK.

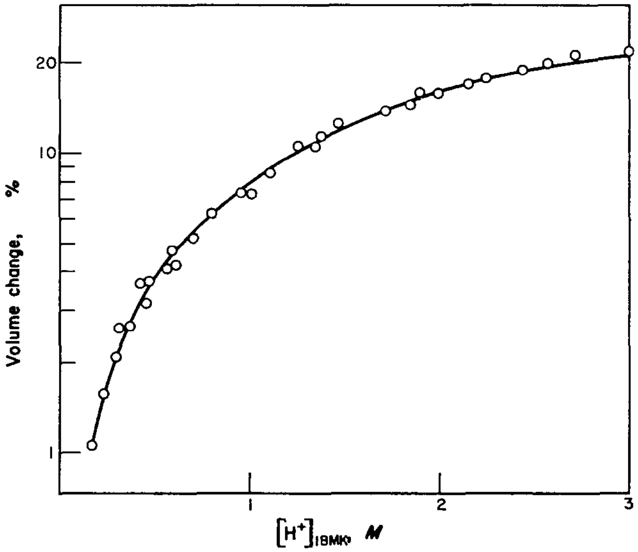

FIG. 1.—Volume change of IBMK as a function of HSCN concentration in the IBMK.

Figure 3 shows a log–log plot of the distribution coefficient of HSCN between IBMK and water *vs.* the equilibrium acid concentration in the aqueous phase. If the HSCN was not solvated by the IBMK in the organic phase, and the activity coefficient of the acid in the aqueous phase remained more or less constant over the concentration range studied, a straight line with a slope of 1 should have been obtained [equation (3)]. The observed deviation of the distribution curve from linearity may then be attributed only to the change in concentration of the solvent and to the second power dependence of the distribution on the solvent concentration, provided the activity coefficient of the HSCN remained constant over the range under investigation.

The equilibrium concentration of IBMK was calculated in the following way; first the decrease in concentration due to the dilution of the IBMK, caused by the volume increase on extraction of HSCN, was considered. At each equilibrium HSCN concentration in the organic phase the volume increase, $a\%$, was read from the curve in Fig. 1, and the resultant concentration of the IBMK $8/(100 + a)$ mole/l. was

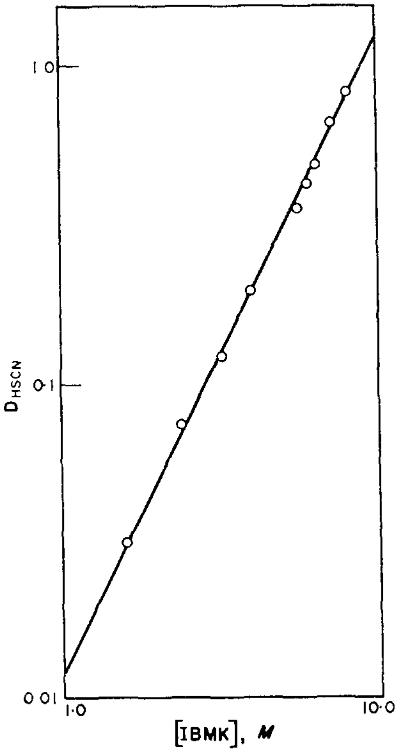

Fig. 2.—The logarithm of the distribution coefficient of HSCN as a function of the logarithm of the IBMK concentration at an equilibrium aqueous HSCN concentration of 0·1*M*.

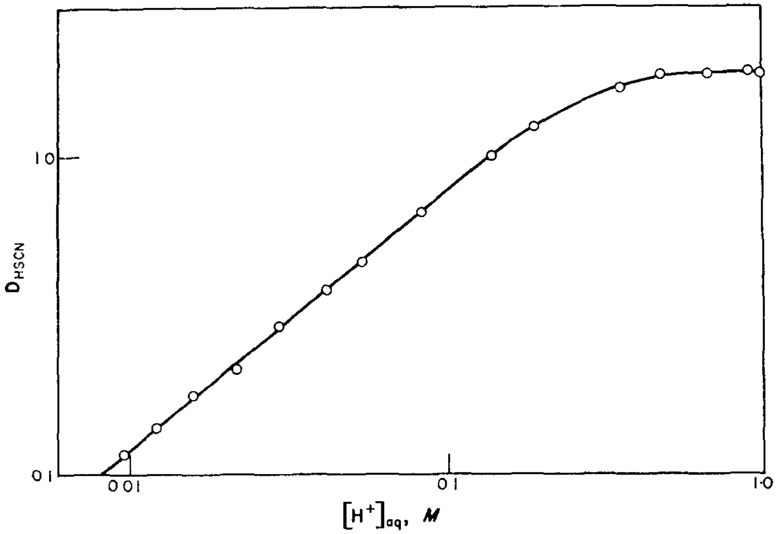

Fig. 3.—Logarithm of the distribution coefficient of HSCN between water and IBMK as a function of the logarithm of the equilibrium aqueous HSCN concentration.

calculated, the concentration of pure IBMK being 8*M*. From the concentration thus obtained, twice the concentration of the HSCN in the IBMK was subtracted, to correct for the IBMK used in the solvation of the acid.

From equation (2) and the corrected concentration values for the solvent, the concentration equilibrium constant for the reaction, as shown in Fig. 4, curve (*a*), was calculated. When the equilibrium constant is plotted as a function of the equilibrium acid concentration in the aqueous phase, a curve similar to the typical activity-coefficient curve for aqueous electrolyte solutions is obtained. However, when the experiments were repeated at a constant ionic strength of 1*M* thiocyanate in the aqueous phase by the addition of NaSCN, an equilibrium constant of 0·114 ± 0·003 [Fig. 4 curve (*b*)], was found for the aqueous acid concentration range 0·01–0·5*M*. This is taken to be a strong indication that the variation of the equilibrium constant [Fig. 4 curve (*a*)], observed in pure HSCN solutions, is solely a function of the change in activity coefficient of the aqueous HSCN.

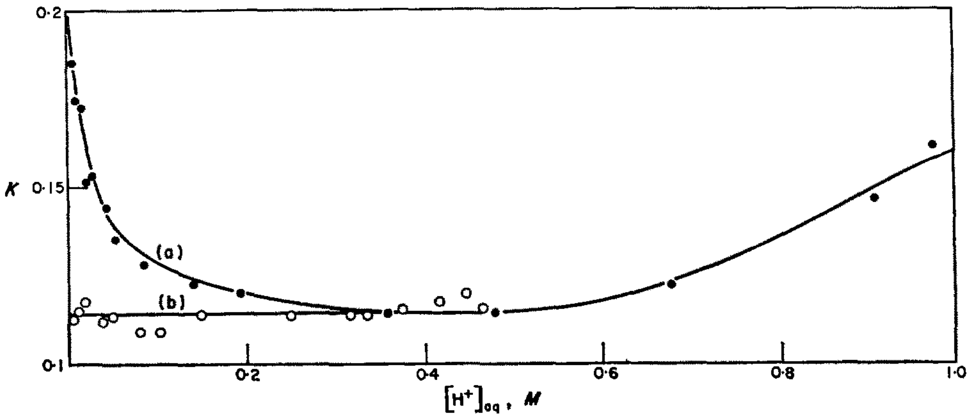

FIG. 4.—Equilibrium constant as a function of the equilibrium aqueous HSCN concentration with IBMK as solvent.
Curve (*a*): with pure HSCN
Curve (*b*): at constant ionic strength of 1*M* thiocyanate.

As IBMK is a polar solvent, the possibility exists that HSCN may dissociate in the solvent. This would give rise to a variation in activity coefficient with variation in acid concentration in the organic phase, and thus also influence the equilibrium constant. In view of the results of Fig. 4 curve (*b*), however, this effect (if present) is negligible.

Xylene system

It is unlikely that any dissociation of HSCN takes place in xylene which is a non-polar solvent. Furthermore, since the concentration of the acid in xylene was always very small because of the low distribution coefficient of HSCN in this system, the activity coefficient of the HSCN in xylene was assumed to be constant.

Two series of extraction experiments were performed on aqueous solutions of HSCN, with xylene as the extractant. Here again the extractions were first performed on pure HSCN solutions. The values of the equilibrium constant obtained are shown as a function of equilibrium aqueous HSCN concentration in Fig. 5 curve (*a*). Again, the typical activity coefficient curve of an electrolyte solution is observed. When the experiments were repeated at a constant thiocyanate concentration of 1*M* in the aqueous phase, the value of the equilibrium constant [Fig. 5 curve (*b*)] was 0·0148 ± 0·0002. This conclusively proves that the deviations observed are only a function of the activity coefficient of the HSCN in aqueous solution.

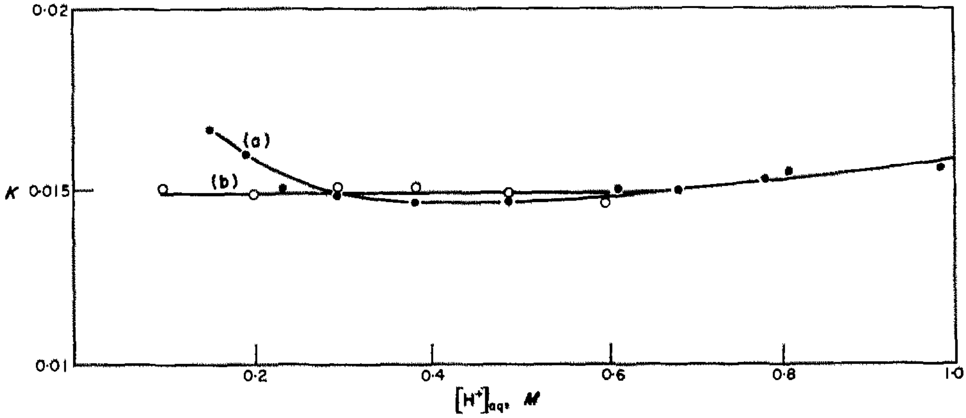

FIG. 5.—Equilibrium constant as a function of the equilibrium aqueous HSCN concentration with xylene as solvent.
Curve (*a*): with pure HSCN
Curve (*b*): at constant ionic strength of 1*M* thiocyanate.

These results clearly show the differences in extraction behaviour of HSCN when polar and non-polar solvents are used. Preliminary results, with alcohols and ethers as solvents, indicate that HSCN is also solvated in these systems but that the solvation number is not necessarily the same as that in IBMK.

Acknowledgements—We wish to thank P. Crowther and M. C. B. Smit for their helpful discussions, and K. S. de Haas for his capable assistance with the experimental work.

Zusammenfassung—Das Extraktionsverhalten von Rhodanwasserstoffsäure in Isobutylmethylketon und Xylol wird beschrieben. Im Keton-system ist die Rhodanwasserstoffsäure in der organischen Phase solvatisiert; für den Komplex wird die Zusammensetzung HSCN·2IBMK vorgeschlagen. Abweichungen vom idealen Verhalten werden gezeigt, die auf eine Änderung des Aktivitätskoeffizienten der Säure in der wäßrigen Phase zurückgeführt werden können.

Résumé—On décrit le comportement à l'extraction par solvant de l'acide thiocyanique avec la méthylisobutylcétone et le xylène comme solvants. Dans le système cétone, l'acide thiocyanique est solvaté dans la phase organique pour donner un complexe pour lequel on propose la composition HSCN, 2IBMK. Il se manifeste des déviations par rapport au comportement idéal, que l'on peut attribuer à des variations du coefficient d'activité de l'acide dans la phase aqueuse.

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SOLVENT EXTRACTION OF HAFNIUM(IV) BY *N*-BENZOYL-*N*-PHENYLHYDROXYLAMINE

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Summary—The extraction of hafnium(IV) tracer by *N*-benzoyl-*N*-phenylhydroxylamine (BPHA) from $1M$ perchloric acid has been investigated and stability constants have been calculated for the complexes $\text{Hf(BPHA)}_i^{(4-i)+}$ ($i = 1 \ldots 4$). It was found that variation of perchlorate concentration in the range $0{\cdot}5$–$2{\cdot}0M$ at constant acidity has no effect on the distribution of hafnium.

It has previously been established that hydroxamic acids possess high complexing power for quadrivalent ions such as zirconium(IV), hafnium(IV) thorium(IV) and plutonium(IV).[1–6] This group of reagents is therefore of particular interest in the investigation of potential separation methods for these elements. Data on the relative stabilities of the metal complexes are necessary for such studies, but are not available in most cases.

Considerable interest in the stability of metal hydroxamate complexes has also arisen due to suggestions[7,8] that radiolytic degradation or nitric acid attack could lead to the formation of hydroxamic acids in some organic diluents used for the recovery of plutonium and uranium from irradiated nuclear fuels. The presence of hydroxamic acids in the organic phase could for example explain the marked zirconium-extracting properties observed in several cases.[8]

The only investigations of the behaviour of zirconium(IV) and hafnium(IV) in aqueous solutions containing hydroxamic acids are those by Baroncelli and Grossi,[2] who determined stability constants for zirconium benzohydroxamates in $1M$ perchloric acid, and by Hála,[6] who examined the extraction mechanism of zirconium(IV) and hafnium(IV) by *N*-benzoyl-*N*-phenylhydroxylamine (BPHA) from strongly acidic ($>6N$) solutions. Although it is known that hafnium(IV) is also extracted from less acidic solutions,[6] the extraction mechanism and the stabilities of the corresponding complexes have not been determined previously. It seemed therefore of interest to investigate in more detail the extraction of hafnium in tracer concentrations from $0{\cdot}5$–$2{\cdot}0M$ perchloric acid.

EXPERIMENTAL

Reagents

Hafnium. Hafnium tracer ($^{175+181}$Hf) in hydrochloric acid solution was obtained from Amersham The solution was twice evaporated with concentrated perchloric acid and a stock solution in $10{\cdot}0M$ perchloric acid was prepared. Tracer solutions for extraction experiments were prepared by diluting the stock solution to $1M$ perchloric acid. The hafnium concentration of these solutions was about $2 \times 10^{-8}M$.

N-Benzoyl-N-phenylhydroxylamine. BPHA (Merck, *pro analysi*) was used as received. The distribution constants K_d between the organic phases and $1M$ perchloric acid were determined spectrophotometrically by measuring the absorbance of BPHA at 255 mμ.

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* Seconded from South African Atomic Energy Board, Pelindaba to U.O.F.S.

All other reagents used in this investigation were of analytical grade. Sodium perchlorate solutions were prepared from perchloric acid and sodium hydroxide. Chloroform was shaken with 1*M* perchloric acid to remove alcohol impurity.

Procedure

Experiments were carried out at 25°. Equal volumes (10·0 ml) of organic and aqueous phases were stirred for 90 min (it was shown experimentally that extraction equilibrium is reached within this time). Organic phases consisted of chloroform solutions of BPHA; aqueous solutions were prepared by diluting 2·0 ml of hafnium tracer (in 1·0*M* perchloric acid) with perchloric acid and sodium perchlorate to the required acidity and ionic strength. After centrifuging, 2·0-ml aliquots of both phases were counted with a well-type scintillation counter. Mass balance was always very good.

RESULTS AND DISCUSSION

Distribution constants

An investigation of the distribution constant of BPHA between 1*M* perchloric acid and benzene as a function of the total BPHA concentration has revealed that the activity of BPHA in the organic phase varies with concentration. A K_d value of 23 was obtained for $[\mathrm{BPHA}]_{tot}$ up to about $1 \times 10^{-3}M$, but this gradually increased with concentration to a value of $K_d = 37$ for $[\mathrm{BPHA}]_{tot} = 6 \times 10^{-2}M$.

The distribution constant for chloroform as organic phase remained essentially constant over the whole range of BPHA concentrations used in this work. This is also supported by the results of Dyrssen.[1] Chloroform was therefore preferred to benzene as solvent in the present investigation. A K_d value of 137 ± 5 was obtained for the distribution of BPHA between chloroform and 1*M* perchloric acid.

Effect of $[\mathrm{ClO_4^-}]$ *and* $[\mathrm{H^+}]$

It has been suggested that hafnium(IV) is extracted into chloroform and benzene as the mixed complex $[\mathrm{Hf(BPHA)}_i(\mathrm{ClO_4})_{4-i}]$ from 0·5–2·0*M* perchloric acid solutions containing BPHA.[6] In an attempt to investigate further the mechanism of this extraction, the effect of perchlorate concentration on the extraction of hafnium from solutions of constant acidity was studied. From the results (Fig. 1, curve 1) it is seen that the distribution ratio of hafnium remains the same when $[\mathrm{H^+}]$ is kept constant at 0·5*M* and $[\mathrm{ClO_4^-}]$ (and thus also the ionic strength) is varied from 0·5 to 2·0*M*. This is not in support of the view that hafnium(IV) is extracted as a mixed complex and would be more in agreement with $\mathrm{Hf(BPHA)_4}$ as the extracted complex.

The dependence of the hafnium distribution on $[\mathrm{H^+}]$ at constant ionic strength ($\mu = 2{\cdot}0$) is shown in Fig. 1, curve 2. The slope of the line is 2·7. Assuming that hafnium was present as free unhydrolysed ions at the start of the extraction (as would be expected for $10^{-8}M$ hafnium solution in 1*M* perchloric acid),[9–13] this slope value could be due to (*i*) the extraction of a mixed BPHA–perchlorate complex, or (*ii*) the formation of the complexes $\mathrm{Hf(BPHA)}_i^{(4-i)+}$ ($i = 1 \ldots 4$) in the aqueous phase with $\mathrm{Hf(BPHA)_4}$ as the extracted complex.

In view of the results obtained here, (*ii*) appears to be more likely. Such an explanation for the slope of curve 2 is also in agreement with the results shown in Fig. 2.

Effect of BPHA concentration

The variation of the extraction of hafnium(IV) with BPHA concentration is shown in Fig. 2 where log *q* (distribution ratio of hafnium) is plotted against log *A*. The

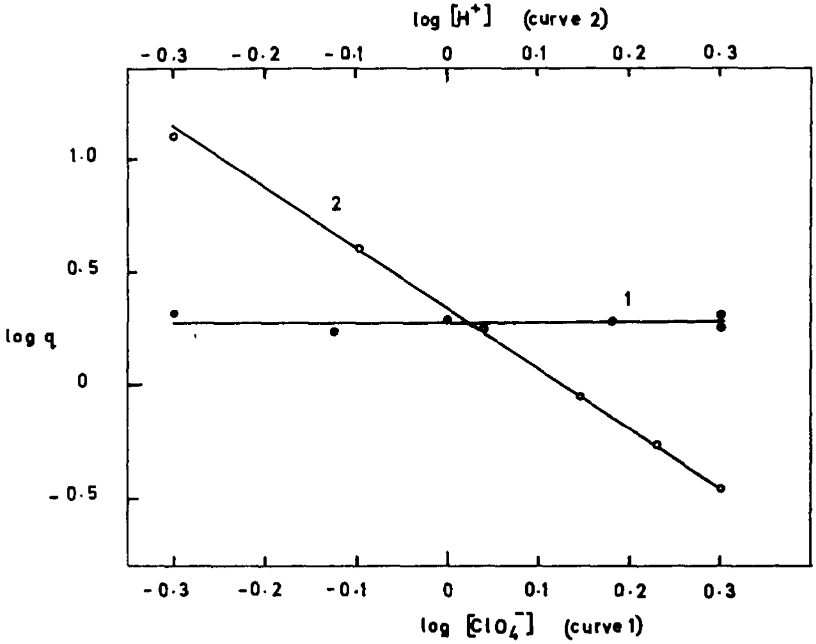

FIG. 1.—Distribution of Hf as a function of $[ClO_4^-]$ and $[H^+]$.
Curve 1: $9{\cdot}78 \times 10^{-4}M$ BPHA, $0{\cdot}5M$ $HClO_4$ + $(M - 0{\cdot}5)NaClO_4$.
Curve 2: $1{\cdot}96 \times 10^{-3}M$ BPHA, $\mu = 2{\cdot}0$ ($HClO_4$ + $NaClO_4$).

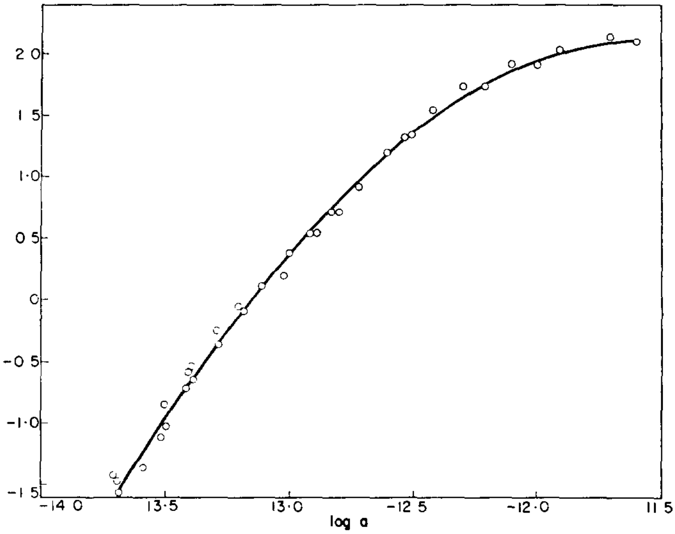

FIG. 2.—Distribution of Hf as a function of the *N*-benzoyl-*N*-phenylhydroxamate ion concentration in $1M$ $HClO_4$.

ligand concentration, A, was calculated from the relationship

$$A = \frac{K_a.[\mathrm{HA}]_0}{[\mathrm{H}^+].K_d}$$

where $[\mathrm{HA}]_0$ is the concentration of BPHA in the organic phase, and K_a is the dissociation constant for BPHA. The experimentally determined value (137) of K_d and Dyrssen's value of K_a, $7{\cdot}08 \times 10^{-9}$, were used.[1] Introduction of this value for K_a could cause a small negative error in the calculated values for A, as Dyrssen's value was determined with a solution of ionic strength 0·1. In view of the magnitude of this effect, it is, however, unlikely that the results will be affected significantly.

The shape of the curve in Fig. 2 (with limiting slope 2·6) is typical of what would be expected if, in addition to the extracted $\mathrm{Hf(BPHA)_4}$ complex, there are also complexes of type $\mathrm{Hf(BPHA)}_i^{(4-i)+}$ ($i = 1 \ldots 3$) present in the aqueous phase.[16] Stability constants calculated by a modification of Leden's[17] extrapolation method and the two-parameter method of Dyrssen and Sillén[18] yielded the following results.

Extrapolation method. The distribution equation[16]

$$q_b = \frac{p_c \beta_c A^c}{\sum\limits_0^N \beta_n A^n} \qquad (1)$$

where q_b denotes the distribution ratio of the metal ion, p_c the distribution ratio of the extracted complex BA_c and $\beta_1 \ldots \beta_N$ the stability constants of the formed complexes, was transformed into the form

$$\frac{A^4}{q_b} = \frac{1}{p_4\beta_4}[1 + \beta_1 A + \beta_2 A^2 + \beta_3 A^3 + \beta_4 A^4] \qquad (2)$$

for the present case where c = N = 4.

A value for p_4 (Table 1) was obtained by extrapolating the function $q_b^{-1}(A^{-1})$ to $A^{-1} = 0$.[19] By successive formation of the functions

TABLE I.—STABILITY CONSTANTS AS CALCULATED BY THE EXTRAPOLATION AND TWO-PARAMETER METHODS

	Extrapolation method	Two-parameter method
$\log p_4$	2·26	2·28
$\log k_1$	13·66	13·78
$\log k_2$	13·24	13·16
$\log k_3$	12·25	12·54
$\log k_4$	12·15	11·92
$\log \beta_4$	51·30	51·40

$$F_0 = \frac{A^4}{q_b}\cdot p_4 = \frac{1}{\beta_4}[1 + \beta_1 A + \beta_2 A^2 + \beta_3 A^3 + \beta_4 A^4]$$

$$F_1 = \frac{\dfrac{A^4}{q_b}\cdot p_4 - \dfrac{1}{\beta_4}}{A} = \beta_1 + \beta_2 A + \beta_3 A^2 + \beta_4 A^3$$

etc., the stability constants $\beta_1 \ldots \beta_4$ were found from $\lim\limits_{A\to 0} F_0$, $\lim\limits_{A\to 0} F_1$, *etc.*

The values for the overall stability constants $\beta_1 \ldots \beta_4$ thus obtained were substituted into equation (2) and were refined by successive approximations until the best fit for the experimental data in Fig. 2 was obtained. These values (Table I, where stepwise stability constants are given) were used to construct the line through the distribution data in Fig. 2.

Two-parameter method. Calculations were carried out according to the method described by Dyrssen and Sillén[18] for the case where $N = 4$. This led to the values $a = 12{\cdot}85$ and $b = 0{\cdot}31$ for the two parameters from which the approximate values for $k_1 \ldots k_4$ in Table I were obtained.

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Zusammenfassung—Die Extraktion eines Hafnium(IV)-Tracers aus $1M$ Überchlorsäure mit *N*-Benzoyl-*N*-phenylhydroxylamin wurde untersucht und für die Komplexe $\mathrm{Hf(BPHA)}_i^{(4-i)}$ ($i = 1 \ldots 4$) Stabilitätskonstanten berechnet. Veränderung der Perchloratkonzentration im Bereich 0,5–2,0M hatte bei konstanter Acidität keinen Einfluß auf die Verteilung von Hafnium.

Résumé—On a étudié l'extraction du traceur hafnium(IV) par la *N*-benzoyl *N*-phénylhydroxylamine (BPHA) à partir d'acide perchlorique $1M$ et l'on a calculé les constantes de stabilité pour les complexes $\mathrm{Hf(BPHA)}_i^{(4-i)}$ ($i = 1 \ldots 4$). On a trouvé qu'une variation de la concentration en perchlorate dans le domaine 0,5–2,0M à acidité constante n'a pas d'influence sur le partage du hafnium.

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APPLICATION OF SOLVENT EXTRACTION TO THE REFINING OF PRECIOUS METALS—III*

PURIFICATION OF GOLD

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Summary—A procedure for the separation of gold from precious metal concentrates, based on its extraction by "dibutyl carbitol", is described. Spectrographic analyses indicate that the resultant metal is of high purity and tests have shown that recovery of the element is essentially quantitative. It appears that advantages could ensue from the incorporation of a scaled-up version of the procedure in an industrial process for the refining of precious metals.

The operations at the International Nickel Refinery at Acton are based entirely on the refining of concentrates of precious metals which are produced during the large-scale extraction of nickel, copper and other elements from ore mined in Canada.[1,2] Consequential amounts of gold and silver are isolated at the refinery in addition to the platinum, palladium, rhodium, ruthenium and iridium.[3] For many important applications the metals are required in a very high state of purity and there is continuous research designed to improve the methods of refining. The present article deals with a laboratory-scale study of a procedure, based on solvent extraction, for the separation of pure gold from the precious metal concentrates.

In the current commercial refining process the concentrate is initially treated with *aqua regia*. Gold, platinum, palladium and base metals dissolve, while rhodium, ruthenium and iridium remain unattacked with the residue of silver chloride formed during the treatment. The gold is recovered by addition of iron(II) sulphate to the solution, which precipitates the metal as a brown sponge. The precipitate of impure gold is melted and cast into anodes for subsequent electrolytic refining. The pure sponge obtained by electrolysis is finally melted and granulated for marketing as gold grain. The resultant metal is of high quality, but the separation and refining have certain disadvantages; the reduction with iron(II) sulphate gives rise to problems with effluent and the electrolysis is time-consuming. These inconveniences are obviated in the method for refining the gold by solvent extraction.

It has long been known that gold(III) may be readily extracted into basic organic solvents from aqueous solutions of hydrochloric acid and this fact has been widely put to use in analytical chemistry for separating the element from many others.[4–7] For the present work "dibutyl carbitol" (diethyleneglycol dibutyl ether, butex) was selected as the extractant. This material has the practical advantages of low volatility (b.p. 254·6°), high flash-point and low solubility in water. Moreover, unlike more basic solvents such as tri-n-butyl phosphate (TBP)[8,9] and tri-n-octyl phosphine oxide (TOPO),[10] dibutyl carbitol does not extract platinum metals from aqueous solutions containing hydrochloric acid.

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* Part II—*Separation Sci.*, 1967, **2**, 635.

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In our method gold(III) is extracted into dibutyl carbitol from the solution resulting from the *aqua regia* treatment of a precious metal concentrate. The organic layer is separated and washed with 1·5*M* hydrochloric acid. The extracted gold is then reduced to metal *in situ* by warming the solvent phase in contact with an aqueous solution of oxalic acid. This reduction in the presence of dibutyl carbitol precipitates the metal in a very well coagulated form. An essentially quantitative recovery of gold is achieved by the procedure and decontamination from other elements is excellent. An important feature of the method is that it separates gold without interfering with the refining of the platinum metals.

EXPERIMENTAL

Solvent

Dibutyl carbitol was obtained from Union Carbide U.K. Ltd. and was always purified before use, as follows. In a separatory-funnel shake 100 ml of the ether with 20 ml of 2% potassium permanganate solution in 1*M* sulphuric acid and drain off the aqueous phase. Repeat this treatment and wash the organic phase with water. Add 100 ml of 30% iron(II) sulphate solution in 1*M* sulphuric acid and leave the phases in contact for 4 hr, changing the ferrous sulphate solution after 3 hr. Run off the aqueous layer, wash the organic phase twice with water and then equilibrate it with 50 ml of 5% sodium carbonate solution for 10 min. Finally agitate the solvent twice for 5-min periods with 4*M* hydrochloric acid.

General procedure

To 15 g of precious metal concentrate add 50 ml of 11·6*M* hydrochloric acid, 5 ml of 16*M* nitric acid and 50 ml of water and digest the mixture overnight on a steam-bath (70–100°). Filter through a sintered glass crucible and wash the residue with 4*M* hydrochloric acid. Make up the filtrate and washings to a volume of 100 ml with 4*M* hydrochloric acid. Transfer the solution to a separatory-funnel and shake it with 100 ml of dibutyl carbitol for 2 min. Drain off and retain the aqueous layer to be worked up for platinum and palladium. Shake the ether layer, which contains the gold, with 25 ml of 1·5*M* hydrochloric acid. Run off the aqueous layer and shake the ether again with two further 25-ml portions of 1·5*M* hydrochloric acid. Discard the aqueous washings.

Run the dibutyl carbitol extract into a beaker containing 100 ml of 5% oxalic acid solution and keep it at 70–80° on a steam-bath for 4–5 hr with occasional stirring to ensure complete reduction of gold to the metallic state. Filter off the metal in a sintered glass crucible and wash it successively with 4*M* hydrochloric acid, water and methylated spirit. Finally ignite the gold to constant weight.

Tests of the efficiency of the procedure

The yield of gold obtained by the procedure was determined by weighing the metal isolated from concentrates which had been analysed previously in more than one laboratory. In addition, yields were determined radiochemically by use of ^{198}Au as a tracer.

The method was tested with two concentrates containing about 5% of gold and having a total precious metal content of *ca.* 70%. Elimination of impurities, achieved by the procedure, was ascertained from spectrographic analyses. Samples of the refined gold (0·2 g) were burned in a graphite electrode, in a 6-A d.c. arc, with the metal in the cathode. Exposures were for 1 min and spectra were recorded on Kodak B 10 photographic plates in a Hilger automatic quartz spectrograph E 742. Spectral line intensities were determined by use of a recording microphotometer and a gold line was used as an internal standard when appropriate.

Measurement of distribution ratios

In the development of the procedure it was necessary to determine the partition behaviour of gold and certain other elements between dibutyl carbitol and hydrochloric acid. Distribution ratios were measured radiochemically at 20° by the usual techniques employed in our laboratory;[11] gold-198, iron-59, arsenic-76, antimony-124 and tin-113 were used as tracers for the respective elements.

RESULTS AND DISCUSSION

In Table I are shown results of determinations of the yield of gold attained by the procedure. From these it can be seen that the recovery of the element from concentrates is almost quantitative.

TABLE I.—DETERMINATION OF THE RECOVERY OF GOLD BY (*a*) GRAVIMETRIC AND (*b*) RADIOCHEMICAL MEASUREMENT

(*a*)	Weight of gold in sample of concentrate taken–based on independent analysis, *g*	Weight of gold recovered, *g*
Concentrate A	0·269	0·2662
	0·268	0·2690
Concentrate B	0·281	0·2815
	0·281	0·2806

(*b*)	Gold-198 activity added to sample of concentrate, *counts*/100 *sec*	Gold-198 activity in recovered gold, *counts*/100 *sec*
Concentrate A	60532	60069
Concentrate B	60080	59560

In these tests the weight of sample taken was ~5 g. The amounts of reagents used in the separations, relative to the weight of concentrate, were the same as described in the general procedure.

The error of the count rates is ±0·4%.

Results of spectrographic analyses of samples of gold separated from two precious metal concentrates by the solvent extraction method are listed in Table II. The analyses indicate that the purity of the product is excellent.

Although it should be emphasized that the present study has been carried out only on a laboratory scale, the results suggest that it could be advantageous to use a scaled-up version of the method in place of the process currently employed in the refining of gold from concentrates of precious metals.

TABLE II.—SPECTROGRAPHIC DETERMINATION OF ELEMENTS IN SAMPLES OF GOLD SEPARATED FROM PRECIOUS METAL CONCENTRATES BY THE SOLVENT EXTRACTION PROCEDURE

Results in %

Trace element	Amount in gold from concentrate A, %		Amount in gold from concentrate B, %	
	1	2	1	2
Pt	n.d.	n.d.	n.d.	n.d.
Pd	n.d.	<0·001	<0·001	<0·001
Rh	<0·001	<0·001	<0·001	<0·001
Ru	n.d.	n.d.	n.d.	n.d.
Ir	0·0027	0·0013	0·0002	0·0005
Ag	0·0005	0·0005	0·0002	0·0002
Sn	n.d.	n.d.	n.d.	n.d.
Mg	<0·0001	<0·0001	<0·0001	<0·0001
Cr	<0·0001	<0·0001	<0·0001	<0·0001
Fe	0·0001	0·0001	0·0001	0·0001
Cu	<0·0001	<0·0001	<0·0001	<0·0001
Si	0·0015	0·0015	0·0018	0·0018
As	<0·001	<0·001	<0·001	<0·001
Pb	0·0001	0·0001	0·0001	0·0001
Sb	<0·001	<0·001	<0·001	<0·001
Zn	<0·0001	<0·0001	<0·0001	<0·0001
Bi	n.d.	n.d.	n.d.	n.d.

n.d. not detected.

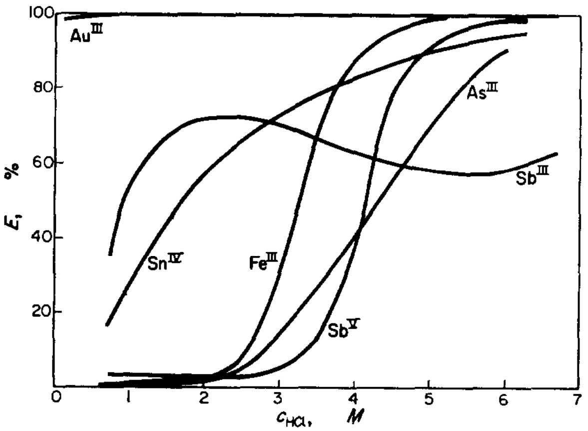

Fig. 1.—The influence of hydrochloric acid concentration on the extraction of chlorides by dibutyl carbitol.
Initial molarities of elements in the aqueous phase: Au(III), $3{\cdot}84 \times 10^{-2}$; Fe(III), $1{\cdot}07 \times 10^{-2}$; As(III), $1{\cdot}60 \times 10^{-2}$; Sb(III), $1{\cdot}80 \times 10^{-3}$; Sb(V), $1{\cdot}80 \times 10^{-3}$; Sn(IV), $9{\cdot}61 \times 10^{-3}$.

Distribution of gold and some other elements between dibutyl carbitol and hydrochloric acid

In the development of our purification method it was necessary to determine the distribution behaviour of gold and certain other elements between dibutyl carbitol and hydrochloric acid. Our experimental results are illustrated in Fig. 1 by the plots of degree of extraction, E, as a function of the hydrochloric acid concentration of the aqueous phase C_{HCl}. The values of E refer to equal volumes of organic and aqueous phase, the dibutyl carbitol having been equilibrated, before use, with aqueous phase with no metal present. For the most part the curves are similar in form to those obtained with diethyl ether as extractant.[4]

Table III.—Variation of distribution ratio D for gold with concentration of the element

C_{HCL}, M	Initial gold(III) concentration of the aqueous phase		
	$6{\cdot}09 \times 10^{-7}M$	$3{\cdot}20 \times 10^{-3}M$	$3{\cdot}84 \times 10^{-2}M$
1	8·28	86·8	464
2	20·8	118	885
3	29·4	295	1820
4	45·6	1065	3166
5	82·0	2590	5380
6	152	4800	10000

It is interesting to note that the distribution ratio

$$D = \frac{\text{Concentration of metal in the organic phase (mole/l.)}}{\text{Concentration of metal in the aqueous phase (mole/l.)}}$$

for gold(III) decreases with diminishing content of the metal, as shown in Table III. Various theories have been advanced to account for this kind of behaviour. A discussion of these is provided in the review by Diamond and Tuck[12] on the extraction of inorganic compounds.

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Zusammenfassung—Es wird ein Verfahren zur Abtrennung von Gold aus Edelmetallkonzentraten beschrieben, das auf der Extraktion mit "Dibutylcarbitol" beruht. Spektrographische Analysen zeigen, daß das gewonnene Metall sehr rein ist. Tests ergaben, daß die Ausbeute des Elements praktisch quantitativ ist. Es erscheint möglich, daß der Einbau des in größeren Maßstab übersetzten Verfahrens in einen industriellen Prozeß bei der Raffination von Edelmetallen Vorteile bringen könnte.

Résumé—On décrit une technique pour la séparation de l'or de concentrats de métaux précieux, basée sur son extraction par le "dibutyl carbitol". Les analyses spectrographiques montrent que le métal résultant est de haute pureté et des essais ont montré que la récupération de l'élément est essentiellement quantitative. Il apparaît que des avantages pourraient découler de l'incorporation d'une version à plus grande échelle de la technique à un procédé industriel de raffinage des métaux précieux.

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SHORT COMMUNICATIONS

The uranium content of sea-water

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THE uranium content of sea-water is of considerable scientific interest to oceanographers. It also has a potential economic interest since all major industrial countries are rapidly becoming committed to nuclear fission as the source of future supplies of electric power and will, if the trend continues, ultimately become wholly dependent on uranium as the nuclear fuel. It is possible that some of the demand could be supplied by thorium but so far no commercial power stations have been built which use thorium-based fuel. The present generation of nuclear power stations requires relatively low-cost uranium (~$10 per lb of U_3O_8) if it is to remain economically competitive, because not more than 3% of the uranium can be consumed. It is confidently expected, however, that before very long these stations will be succeeded by so-called fast breeder reactors which should utilize 60–70% of the uranium. In this case, the cost of the uranium becomes only a small fraction of the total generating cost and a much higher price could be paid before it materially affected the cost of power. At the present time uranium is produced from low-grade ores containing between 0·05 and 0·5% U_3O_8. Known reserves are limited but it it expected that prospecting will establish further reserves. If new discoveries do not keep pace with demand, still lower-grade ores will have to be worked and the price of uranium will rise substantially. The possibility of extracting uranium from sea-water was first considered at Harwell about 1952[1] when complexing agents, such as dibutyl phosphate, with a high specificity for uranium became available. This reagent had been used analytically at the Windscale Laboratories for the determination of the uranium content of a sample of Irish Sea water taken off the Cumberland coast.[2] Earlier determinations had shown considerable variation in uranium content of samples from different places and from different depths. Hernegger and Karlik[3] had applied the fluorimetric method to samples taken in Swedish waters. Values as low as 0·36 μg/l. had been obtained for surface water and 0·98–1·00 μg/l. for water sampled at depths between 60 and 500 m. In a subsequent paper,[4] values between 2·0 and 2·2 μg/l. were quoted for sample from coastal and ocean waters. A number of other workers[5,6] had also reported results lying in a similar range but Nakanishi[7] had found as much as 3·37 μg/l. in a sample taken from the Kuroshio current off the coast of Japan. He estimated the average for deep ocean water to be 2·82 μg/l.

In the first experiments at Harwell,[8] continuous counter-current extraction with two rotary columns operating on a total reflux basis was used to separate uranium from 20 l. of sea-water from Weymouth Bay. Sea-water entered the top of column A where it was mixed with a counter-current flow of dibutyl phosphate (DBP) in kerosene or Butex. The organic phase overflowed through a side-tube at the top of column A and entered the bottom of column B where both the uranium and the DBP were stripped from the kerosene by a counter-current flow of 0·32N sodium carbonate. This aqueous extract was then added to the sea-water feed to column A together with a slight excess of nitric acid. Thus the uranium and the DBP were retained in the system until extraction was complete. The uranium content of the final concentrate was determined by fluorimetric analysis. In two runs, each using 20 l. of sea-water, 60 μg were obtained in one case and 50 μg in the other, corresponding to 3 and 2·5 μg of uranium per litre. Batch determinations on the same sea-water gave a value of 3·0 ± 0·5 μg/l.

Concentration of the uranium by extraction with DBP was also used by Stewart and Bentley[9] but the final determination was by fission-counting after the sample had been irradiated in the Argonne Laboratory heavy water reactor. The mean of ten determinations on two samples taken from Pacific coast surf was 2·49 μg/l. The evidence in favour of a rather higher value was strengthened by the publication in 1956 of a very careful study by Rona, Gilpatrick and Jeffrey[10] at Oak Ridge National Laboratory. Samples were collected from the North Atlantic, North Pacific, Gulf of Mexico and the Florida Straits and were stored and shipped in polythene carboys. The uranium analyses were carried out in laboratories reserved for sea-water experiments, where special precautions were taken against contamination. By using the isotopic dilution mass spectrometric technique of analysis, any error due to loss of uranium in the concentration process was eliminated. A standard "spike" of ^{235}U was added to the sea-water sample before extraction with diethyl hydrogen phosphate in carbon tetrachloride. Quantitative extraction was not essential since results depended on an accurate mass spectrometric determination of the isotopic ratio. Nevertheless the yield at each step of the chemical process was first checked by a tracer experiment with ^{233}U. Blank determinations were also performed with pure water to which the standard spike was added in order to check contamination by uranium from reagents or glassware. Highest values were obtained for surface waters from the Gulf of Mexico (3·43–3·57 μg/l.) and lowest values for Gulf of Mexico samples taken from depths between 600 and 2000 m (3·10–3·32 μg/l.) Samples from the surface waters of the Atlantic and the Pacific gave results lying between these two extremes, the overall average being 3·31 μg/l.

The evidence for a fairly constant value in the neighbourhood of 3 μg/l. now seemed strong but the fact that different methods had given different results led Smales and his collaborators Wilson, Webster, Milner and Barnett[11] to make a comparison of three different methods. These were the isotope dilution method, the fluorimetric method and a new polarographic method.[12] Chemical yields were determined by tracer experiments with ^{235}U for the isotope dilution method and ^{237}U for the fluorimetric and polarographic methods although these experiments were of secondary importance in the case of isotope dilution, where it was only necessary to check that the conditions for the blanks were the same as in the actual determinations.

Two different methods of chemical concentration were used in the isotope dilution experiments, one depending on co-precipitation with aluminium phosphate and the other on extraction of the 8-hydroxyquinoline (oxine) complex with chloroform. The oxine method was also used in the concentration process preparatory to fluorimetric analysis and in this case the yield corrections determined by the ^{237}U tracer method were important, since yields as low as 74% were recorded. For the polarographic determination diethylhexyl phosphoric acid was used in preference to oxine in the preliminary concentration and further special precautions were taken to eliminate possible interfering ions; the yield at each stage was also determined by means of ^{237}U as before.

All three methods gave the same result within the limits of experimental error not only for the same water but for all samples. These originated from Weymouth Bay and from various depths between 7 and 4210 m in the Bay of Biscay. The overall average value was found to be 3·33 ± 0·08 μg/l., in good agreement with that found by Rona, Gilpatrick and Jeffrey[10] (3·39 μg/l.) for waters of the North Atlantic and the Gulf of Mexico. The evidence afforded by this work therefore indicates very strongly that the uranium content of normal sea-water is constant, within the limits of experimental error, irrespective of location and depth. This conclusion is supported by the earlier results of Miss G. Koczy[6] (1950) who carried out 36 determinations on samples obtained from a world wide selection of sites and from a range of depths from 0 to 7500 m. It seems likely that there was a constant error in the fluorimetric method which she used, but all 36 results fell within the range 1·0–1·4 μg/l.

More recent work by Miyake and Sugimura[13,14] gave overall average values for the uranium content in agreement with those reported by Smales and collaborators and Rona *et al.* but showed much wider variation both with location and with depth (1·6–4·7 μg/l.). Chemical concentration stages and a final colorimetric measurement were used. Blank experiments were made but tracer determinations of chemical yield were not carried out. Moreover, the sea-water samples, which were collected in glass bottles, were not acidified, so losses may have occurred in some cases owing to adsorption (see G. Koczy[6]). The variations noted by Miyake and Sugimura must therefore be regarded with some doubt, bearing in mind that the extremely rigorous determinations by Rona, Gilpatrick and Jeffrey and by Wilson, Webster, Milner, Barnett and Smales gave a much narrower range of values.

The mean concentration of uranium in sea-water now seems well established but more determinations by the most rigorous analytical techniques are desirable in order to determine whether significant variations do occur. Of the trace elements present in sea-water, uranium is the only one which might achieve a high enough market price in the foreseeable future[15] to make extraction a commercially attractive possibility. Gold has been a recurrent subject for discussion in this connection ever since Haber's investigations[16] after the first world war. Haber's results were criticized by some authors in the years which followed but his work was to a large extent vindicated by R. W. Hummel (1957)[17] working in the laboratory of A. A. Smales. The gold content of samples of surface and sub-surface water collected from the English Channel and the Bay of Biscay was determined by radioactivation analysis. Hummel, following Haber, attributed the higher gold content found for coastal waters (up to 500 μg/m³) to association of the gold with suspended particulate matter and found that the content of true ocean water was only 15 μg/m³, *i.e.*, less than one thousandth of the uranium content.

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Summary—A review of the literature on the uranium content of sea-water.

Zusammenfassung—Es wird eine Übersicht über die Literatur zum Urangehalt von Meerwasser gegeben.

Résumé—Une revue de la littérature sur la teneur en uranium de l'eau de mer.

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Stability constants of manganese(II) bromide complexes

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PROCEDURES using radiotracers are frequently of great value in the investigation of complex formation and the determination of stability constants. Such methods may often be used in cases where spectrophotometric and potentiometric studies will not yield unequivocal results. The measurement of the activity of a radioactive tracer is usually straightforward, and if a carrier-free radionuclide is available, studies can be made without correction for the amount of complexing ligand bound to the ion under investigation. Moreover, with the low concentrations of the element that can be detected, the possibility of polynuclear complex formation is greatly reduced.

In the present investigation, carrier-free ^{54}Mn was used, together with a cation-exchange resin, to determine stability constants of manganese(II) bromide complexes. The resin, Amberlite IR-120, was used in the H^+-form and the ionic strength of the solutions was maintained at 0·691*M* with perchloric acid. The equilibrium distribution of radiomanganese between the ion-exchanger and the solutions at 20° has been determined by γ-ray scintillation counting. The conditions used were essentially similar to those used in a study of manganese(II) chloride complexes,[1] and the results obtained for the two systems should be directly comparable.

The radionuclide ^{54}Mn has a half-life of 314 days. It decays by electron-capture (100%) to ^{54}Cr and the disintegrations involve the emission of 0·84-MeV γ-rays (100%).

Calculation of stability constants from cation-exchange data

The following notation is used:[2]

C'_{Mn}, C'_{Br} = total concentrations (mole/l.) of manganese and bromide in solutions before addition of the ion-exchange resin

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[M] = equilibrium concentration of a species in aqueous solution

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[M] = equilibrium concentration of a species in aqueous solution

$[\mathrm{M}]_\mathrm{R}$ = equilibrium concentration of a species in the resin phase (mole/g of dry resin)

$\beta_j = \dfrac{[\mathrm{MnBr}_j^{(2-j)+}]}{[\mathrm{Mn}^{2+}][\mathrm{Br}^-]^j}$, *the stability constant of the complex* $\mathrm{MnBr}_j^{(2-j)+}$

$\lambda_j = \dfrac{[\mathrm{MnBr}_j^{(2-j)+}]_\mathrm{R}}{[\mathrm{MnBr}_j^{2-j+}]}$; $(j = 0, 1)$

$\lambda_j' = \beta_j \cdot \dfrac{\lambda_j}{\lambda_0}$; $(j = 1)$

v = initial volume of the solution
m = weight of dry resin used
δ = swelling factor of the ion exchanger

$$X = 1 + \sum_{j=1}^{n} \beta_j[\mathrm{Br}^-]\ ;\ X_j = (X_{j-1} - \beta_{j-1})/[\mathrm{Br}^-];\ (X_0 = X;\ \beta_0 = 1).$$

For the determination of the stability constants β_j, the functions ϕ_1 and f, due to Fronaeus, were used. For further details see references 1–3.

$$\phi = \frac{(\mathrm{C}_{Mn})_\mathrm{R}}{\mathrm{C}_{Mn}} = \frac{v}{m}\left(\frac{\mathrm{C}_{Mn}'}{\mathrm{C}_{Mn}} - \delta\right) = \lambda_0(1 + \lambda_1'[\mathrm{Br}^-])/X \tag{1}$$

$$\phi_1 = \left(\frac{\lambda_0}{\phi} - 1\right) \cdot \frac{1}{[\mathrm{Br}^-]} \tag{2}$$

$$\begin{aligned} f &= \left\{\frac{\lambda_0}{\phi}\,[(\beta_1 - \lambda_1')[\mathrm{Br}^-] - 1] + 1\right\} \cdot \frac{1}{[\mathrm{Br}^-]^2} \\ &= \frac{\beta_1(\beta_1 - \lambda_1') - \beta_2 + [\mathrm{Br}^-]\{X_2(\beta_1 - \lambda_1') - X_3\}}{(1 + \lambda_1'[\mathrm{Br}^-])} \end{aligned} \tag{3}$$

$$\phi_1^\circ = \lim_{[\mathrm{Br}^-]\to 0} \phi_1 = \beta_1 - \lambda_1' \tag{4}$$

$$f^\circ = \lim_{[\mathrm{Br}^-]\to 0} f = \beta_1\phi_1^\circ - \beta_2 \tag{5}$$

$$\Delta\phi_1 = \phi_1 - \phi_1^\circ \tag{6}$$

$$\Delta f = f - f^\circ \tag{7}$$

The stability constants can be determined from the relationship

$$\frac{\Delta f}{[\mathrm{Br}^-]} = \beta_1 \cdot \frac{\Delta\phi_1}{[\mathrm{Br}^-]} - \beta_3 - \beta_4[\mathrm{Br}^-] \tag{8}$$

and equations (4) and (5).

EXPERIMENTAL

The experimental method was similar to that used by Morris and Short[1] for the determination of stability constants of manganese(II) chloride complexes.

The manganese concentrations of the resin phases $(\mathrm{C}_{Mn})_\mathrm{R}$ and of the aqueous phases C_{Mn} at equilibrium were determined from measurements of the count rates of aliquots of solution before addition of ion-exchanger and after equilibrium had been obtained. A NaI(Tl) scintillation counter was used for the measurements of activity.

RESULTS AND DISCUSSION

The results for the effect of hydrobromic acid concentration on the distribution ratio of radiomanganese, and the functions used in evaluating stability and other constants, are given in Table I. The magnitudes ϕ_1 and f were plotted *vs.* $[\mathrm{Br}^-]$ and extrapolated to $[\mathrm{Br}^-] = 0$ to give ϕ_1° and f°. The stability constant β_1 could be evaluated from the slope of the plot of $\Delta f/[\mathrm{Br}^-]$ against $\Delta\phi_1/[\mathrm{Br}^-]$ shown in Fig. 1. The fact that the graph is a straight line passing through the origin indicates that under the conditions of the experiment both β_3 and β_4 are essentially equal to zero. The value of β_2 was obtained from equations (4) and (5).

TABLE I.—EFFECT OF THE HYDROBROMIC ACID CONCENTRATION ON THE CATION-EXCHANGE DISTRIBUTION

$[Br^-]$, *M*	ϕ, *l./g*	ϕ_1, $(mole/l.)^{-1}$	f, $(mole/l.)^{-2}$	$\Delta\phi_1/[Br^-]$, $(mole/l.)^{-2}$	$\Delta f/[Br^-]$, $(mole/l.)^{-3}$
0	0·1527	(0·4495)	(−0·1746)	—	—
0·03599	0·1502	0·4625	−0·1502	0·3612	0·6782
0·07198	0·1477	0·4742	−0·1295	0·3432	0·6366
0·1080	0·1451	0·4850	−0·1080	0·3287	0·6267
0·1440	0·1426	0·4944	−0·08988	0·3118	0·5882
0·1800	0·1400	0·5040	−0·07410	0·3028	0·5583
0·2159	0·1375	0·5120	−0·05952	0·2895	0·5331
0·2520	0·1350	0·5193	−0·04420	0·2770	0·5175
0·2879	0·1326	0·5265	−0·03081	0·2675	0·4995
0·3229	0·1303	0·5332	−0·01965	0·2592	0·4800
0·3600	0·1279	0·5400	−0·008465	0·2514	0·4614
0·3959	0·1256	0·5450	0·003808	0·2412	0·4506
0·4319	0·1234	0·5497	0·01500	0·2320	0·4390
0·5039	0·1191	0·5599	0·03261	0·2191	0·4112
0·5758	0·1150	0·5693	0·04778	0·2081	0·3862

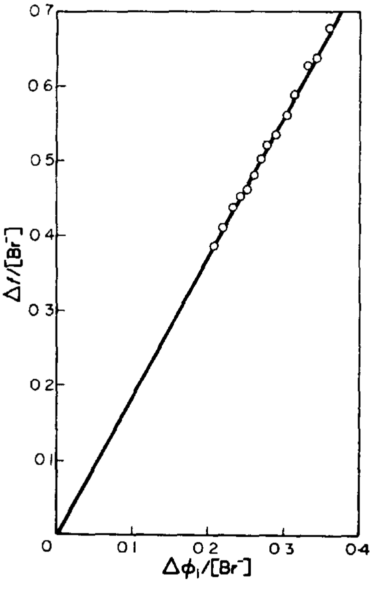

FIG. 1.—Evaluation of stability constants for the manganese(II) bromide system.

Final values obtained for the overall stability constants β_j and the step constants $K_j = \beta_j/\beta_{j-1}$ at 20° and an ionic strength of 0·691*M* (HBr and $HClO_4$) are: $\beta_1 = 1·85 \pm 0·1$; $\beta_2 = 1·01 \pm 0·2$; $K_1 = 1·85$; $K_2 = 0·55$.

In the case of manganese(II) it appears that the bromide complexes are weaker than the corresponding chloride complexes; this corresponds to (*a*)-behaviour in Ahrland's classification.[4,5]

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Summary—Manganese-54 has been used as a tracer in an investigation of solutions containing manganese(II) bromide complexes. By a cation-exchange method values have been obtained for the stability constants $\beta_j = [MnBr_j^{(2-j)+}]/[Mn^{2+}][Br^-]^j$, valid for 20° and ionic strength $0{\cdot}691M$ maintained with perchloric acid.

Zusammenfassung—Mangan-54 wurde bei einer Untersuchung von Lösungen, die Mangan (II)-Bromidkomplexe enthielten, als Tracer verwendet. Mit einer Kationenaustauschmethode wurden Werte der Stabilitätskonstanten $\beta_j = [MnBr_j^{(2-j)+}]/[Mn^{2+}]\ [Br^-]^j$ ermittelt, die für 20° und eine mit Überchlorsäure eingestellte Ionenstärke 0,691 gelten.

Résumé—On a utilisé le manganèse-54 comme traceur dans une recherche sur des solutions contenant des complexes du bromure de manganèse (II). Par une méthode d'échange cationique, on a obtenu des valeurs pour les constantes de stabilité $\beta_j = [MnBr_j^{(2-j)+}]/[Mn^{2+}]$ $[Br^-]^j$, valable pour 20° et une force ionique $0{,}691M$ maintenue par l'acide perchlorique.

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Spectrophotometric determination of platinum in experimental catalysts

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A METHOD was required in our laboratories for the determination of small amounts of platinum in a variety of experimental catalysts which contained no other platinum metals, but large amounts of other metals. In most cases only a limited amount of sample was available.

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EXPERIMENTAL

Reagents

All reagents were of the highest purity available and distilled or demineralized water was used throughout. Standard platinum solutions were made by dissolving assayed chloroplatinic acid (or that obtained from pure platinum) in $0{\cdot}1M$ hydrochloric acid to give a platinum concentration of 1 mg/ml, and diluting this solution 10- and 100-fold with $0{\cdot}1M$ hydrochloric acid. Tin(II) chloride solution was freshly prepared as required, by dissolving 23 g of the dihydrate in 25 ml of conc. hydrochloric acid, with gentle warming if necessary, cooling, and diluting to 100 ml.

Procedure

Dissolve a suitable weight of sample (60-mesh), preferably containing 0·25–1·5 mg of platinum, in *aqua regia* in a 150-ml tall-form beaker. Evaporate the solution just to dryness on a steam-bath, moisten the residue with conc. hydrochloric acid and evaporate again. Repeat this step then add

Summary—Manganese-54 has been used as a tracer in an investigation of solutions containing manganese(II) bromide complexes. By a cation-exchange method values have been obtained for the stability constants $\beta_j = [\mathrm{MnBr}_j^{(2-j)+}]/[\mathrm{Mn}^{2+}][\mathrm{Br}^-]^j$, valid for 20° and ionic strength 0·691*M* maintained with perchloric acid.

Zusammenfassung—Mangan-54 wurde bei einer Untersuchung von Lösungen, die Mangan (II)-Bromidkomplexe enthielten, als Tracer verwendet. Mit einer Kationenaustauschmethode wurden Werte der Stabilitätskonstanten $\beta_j = [\mathrm{MnBr}_j^{(2-j)+}]/[\mathrm{Mn}^{2+}]\,[\mathrm{Br}^-]^j$ ermittelt, die für 20° und eine mit Überchlorsäure eingestellte Ionenstärke 0,691 gelten.

Résumé—On a utilisé le manganèse-54 comme traceur dans une recherche sur des solutions contenant des complexes du bromure de manganèse (II). Par une méthode d'échange cationique, on a obtenu des valeurs pour les constantes de stabilité $\beta_j = [\mathrm{MnBr}_j^{(2-j)+}]/[\mathrm{Mn}^{2+}]\,[\mathrm{Br}^-]^j$, valable pour 20° et une force ionique 0,691*M* maintenue par l'acide perchlorique.

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Spectrophotometric determination of platinum in experimental catalysts

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A METHOD was required in our laboratories for the determination of small amounts of platinum in a variety of experimental catalysts which contained no other platinum metals, but large amounts of other metals. In most cases only a limited amount of sample was available.

A modification of the tin(II) chloride colorimetric method was made and shown to meet the requirements. Various workers[1-6] have investigated this method, and while most conclude that relatively high acidities are preferable, there is no general agreement on the best conditions. Extraction of the platinum–tin(II) complex makes the method more selective, and a number of solvents have been proposed[1,5,7-9] but it is necessary to use additional reagents or operations to improve the phase separation or the stability of the extracted colour. We have re-examined the system and have found that isoamyl alcohol is a better solvent than any hitherto proposed.

EXPERIMENTAL

Reagents

All reagents were of the highest purity available and distilled or demineralized water was used throughout. Standard platinum solutions were made by dissolving assayed chloroplatinic acid (or that obtained from pure platinum) in 0·1*M* hydrochloric acid to give a platinum concentration of 1 mg/ml, and diluting this solution 10- and 100-fold with 0·1*M* hydrochloric acid. Tin(II) chloride solution was freshly prepared as required, by dissolving 23 g of the dihydrate in 25 ml of conc. hydrochloric acid, with gentle warming if necessary, cooling, and diluting to 100 ml.

Procedure

Dissolve a suitable weight of sample (60-mesh), preferably containing 0·25–1·5 mg of platinum, in *aqua regia* in a 150-ml tall-form beaker. Evaporate the solution just to dryness on a steam-bath, moisten the residue with conc. hydrochloric acid and evaporate again. Repeat this step then add

20 ml of hydrochloric acid (1 + 1) and warm to dissolve soluble salts (Note 1). Cool, and add 20 ml of the tin(II) chloride reagent (Note 2). Transfer to a 100-ml volumetric flask, dilute to the mark, and mix well. Let stand for 10 min and then *either* measure the absorbance at 403 mμ in a 1-cm cell against a reagent blank *or* transfer 50·0 ml of the solution to a 250 ml separating funnel, extract for 1 min with exactly 50·0 ml (for 0–1 mg of Pt) or 10·0 ml (for 0–0·125 mg) of isoamyl alcohol, let stand for 1 min, run off and discard the lower (aqueous) layer, filter through a small dry Whatman No. 541 paper into a 1-cm cell, and measure the absorbance at 399 mμ against a reagent blank. Prepare appropriate calibration curves in the usual way.

Notes. 1. Insoluble matter such as silica is best filtered off before addition of the tin(II) reagent. 2. If any iron present is in the reduced state it is not necessary to use solvent extraction to eliminate its interference, but to hasten its reduction it is advisable to warm the solution to about 60° for a few minutes after addition of the tin(II).

RESULTS AND DISCUSSION

In aqueous medium the complex has an absorption spectrum with a broad peak at 403 mμ. The colour is stable for at least 24 hr. The tin(II) concentration can be varied from 0·04 to 0·25*M* in the final solution, and the final hydrochloric acid concentration from 1·1 to 3·3*M*, without influencing the colour, but if the hydrochloric acid is less than 1·1*M*, some tin may be precipitated. Beer's law is obeyed at 403 mμ over the range 0–2 mg of platinum in 100 ml of final solution.

Investigation of the effect of other metals known to be present in the catalysts showed that in the determination of 1 mg of platinum the following metals caused no interference when present at the levels indicated (mg): Cu (100), Fe (1000), Mn (100), Zn (100), Na (2000), K (75), Cu + Zn (50 + 50); NH_4^+ (1500) also did not interfere; Cu (500) and Fe (1000) did not interfere when 2 mg of platinum were determined. Of the metals examined, only Cr, Ni and Mo interfered. The effect of molybdenum was of interest and was studied more closely. Under the test conditions molybdenum gave a brown solution with λ_{max} 390 mμ. The absorbance at 403 mμ followed Beer's law and 33 mg of molybdenum gave the same absorbance as 0·5 mg of platinum. A correction may be applied if the molybdenum content is known, or platinum can be extracted and determined and the molybdenum obtained by difference.

The absorption spectrum of the extracted platinum complex is very similar to that of the complex in aqueous solution, the maximum being shifted slightly to 399 mμ. The colour of the extract is stable for at least 24 hr. Phase separation is clean and complete within 1 min, with no emulsion formation, and a single extraction with equal volumes of the two phases removes >99% of the

TABLE I.—ELIMINATION OF INTERFERENCE FROM OTHER METALS BY SOLVENT EXTRACTION TECHNIQUE FOR DETERMINATION OF PLATINUM

Metal	Present in 100 ml aqueous solution, *mg*		Absorbance, 1-*cm*		Pt recovered in organic phase, *mg*
	Metal	Pt	aqueous, 403 mμ	isoamyl alcohol, 399 mμ	
—	—	Nil	Nil	Nil	—
—	—	1·00	0·410	0·398	—
Mo	66	Nil	0·409	0·004	0·01
Mo	66	1·00	0·815	0·400	1·00
Mo	330	Nil	>2·0	0·004	0·01
Mo	330	1·00	>2·0	0·406	1·02
Cr	40	1·00	0·505	0·398	1·00
Cr	80	1·00	0·605	0·398	1·00
Ni	100	1·00	0·499	0·398	1·00
Ni	500	1·00	0·795	0·395	0·99
Mo Cr Fe	66 100 100	1·00	1·00	0·400	1·00
—	—	2·00	0·815	0·780	—
Mo	66	2·00	1·25	0·781	2·00
Mo	330	2·00	>2·0	0·780	2·00
Cr	500	2·00	>2·0	0·775	1·99
Fe	1000	2·00	0·810	0·780	2·00

platinum. Equilibrium is reached with 1 min of shaking. Beer's law is obeyed by the extract, but the sensitivity depends on the ratio of the phase volumes, a considerable improvement in sensitivity being obtained by extracting into a smaller volume. The solvent extraction procedure eliminates the interference of nickel, chromium and molybdenum and there is no interference from the other elements tested (see Table I).

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Summary—Conditions have been established and procedures are described for the colorimetric determination of platinum in experimental catalysts and miscellaneous materials. The methods are based on the measurement of the intensity of colour produced by the reaction of chloroplatinic acid with tin(II) chloride. Interference from metals such as chromium, molybdenum and nickel, which are often also present in catalysts, is overcome by selective extraction of the complex into isoamyl alcohol followed by measurement of the absorbance of the alcohol layer.

Zusammenfassung—Die Arbeitsbedingungen zur kolorimetrischen Bestimmung von Platin in Versuchskatalysatoren und verschiedenen Materialien wurden ermittelt und Arbeitsvorschriften mitgeteilt. Die Vorschriften beruhen auf Messung der Intensität der Färbung, die sich bei der Reaktion von Chloroplatinsäure mit Zinn(II) chlorid entwickelt. Störungen durch Metalle wie Chrom, Molybdän und Nickel, die ebenfalls oft in Katalysatoren vorkommen, werden beseitigt, indem man den Komplex selektiv in Isoamylalkohol extrahiert und dann die Extinktion der Alkoholschicht mißt.

Résumé—On a établi les conditions et l'on décrit des techniques pour le dosage colorimétrique du platine dans des catalyseurs expérimentaux et divers produits. Les méthodes sont basées sur la mesure de l'intensité de coloration produite par la réaction de l'acide chloroplatinique avec le chlorure stanneux. L'interférence de métaux tels que le chrome, le molybdène et le nickel, qui sont souvent également présents dans les catalyseurs, est évitée par l'extraction sélective du complexe en alcool isoamylique suivie de la mesure de l'absorption de la couche alcoolique.

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TALANTA REVIEW*

DETERMINATION OF ANTIOXIDANTS IN POLYMERIC MATERIALS

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Summary—A review of methods proposed for the analysis of antioxidants in polymeric materials, cast in the form of a step-by-step examination of the problems involved in any scheme of analysis, with a critical appraisal of the published procedures designed to overcome them.

THE range of applications for polymeric materials is still increasing at an enormous rate, and as it does so, the number of additives available to modify polymer properties increases proportionately. Inevitably, the problems associated with polymer analysis for minor components have become correspondingly complex, whilst the need for such analysis is more urgent than ever, particularly in connection with medical plastics and food packaging where the identities and levels of potentially toxic substances must be accurately known and controlled.

The development of an analytical scheme comprehensive enough to cover all types of polymer additive would be an extremely lengthy undertaking (even if it should prove possible) but a scheme sufficient to identify and determine most currently available antioxidants should be attainable, and this review is designed to provide the necessary background on which to base it.

In order to appreciate fully the techniques which have been developed for the analysis of antioxidants in polymers, it is necessary to be familiar with the difficulties involved in such an undertaking, and also with the chemical properties of antioxidants themselves.

Most of the analytical problems arise from three factors; the situation of the antioxidant in a more or less insoluble polymer matrix, the high reactivity and low stability of antioxidants, and the low concentrations of antioxidants present (0·01–1·0%). The first severely limits the analytical techniques which can be applied to the sample without prior separation of the antioxidant from polymer, a procedure which is itself hindered by the nature of the polymer matrix. In addition, any extract is liable to contamination by low molecular weight polymer "wax" which may interfere with subsequent treatment and is difficult to remove.

The second and third factors combine to make the handling of extracts an exacting job if quantitative information is required. Antioxidants are labile unstable compounds forming complex decomposition products; this considerably complicates interpretation of analytical data, and any loss of material is liable to be significant since the quantities of antioxidants present are initially so low. Crompton,[1] for example,

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* For reprints of this Review see advertisement in this issue.

recommends that extracts should be kept in smoked glassware and used for subsequent analysis without delay. If any storage of solutions is necessary, this should be done under nitrogen, in the dark and in a refrigerator. Lorenz *et al.*[2] have published data on sample changes during processing of antioxidant extracts, including losses during concentration by evaporation. Generally, however, this aspect of antioxidant analysis does not seem to have received the consideration it deserves.

Apart from these factors which complicate the processing of the sample, there are others which complicate the interpretation of the data obtained, the principal ones being the wide range of antioxidants available, which makes positive identification difficult, the presence of other types of additive (plasticizers, UV-stabilizers, slip-agents and the like) and possibly the presence of more than one antioxidant with its associated decomposition products, depending on the age of the sample (irrespective of decomposition caused by analytical processing).

It should also be noted, however, that there are at least two factors which operate on behalf of the analyst, namely the limited number of molecular types which may be used as antioxidants, and the chemical reactivity of these types.

THE FUNCTION AND NATURE OF ANTIOXIDANTS

It is generally accepted that autoxidation of polymeric materials proceeds *via* a free radical mechanism involving molecular oxygen.[3,4] One of the paths of autoxidation might be represented thus:

$$\begin{aligned} R + O_2 &\longrightarrow RO_2\cdot \\ RO_2\cdot + RH &\longrightarrow ROOH + R\cdot \end{aligned}$$

where R· represents a free radical formed by the decomposition of the polymeric species RH. The inhibitory action of antioxidants depends on their ability to interrupt this chain process by forming a non-propagating free radical thus:

$$\begin{tikzcd} R\cdot + O_2 \arrow[r] & RO_2 \\ RO_2 + AH \arrow[r] & ROOH + A\cdot \arrow[d] \\ & \text{stable products} \end{tikzcd}$$

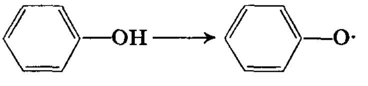
All currently used inhibitor molecules AH have the following properties.

(*a*) A labile hydrogen atom, (in fact, antioxidant activity is directly related to the A—H bond dissociation energy[5]).

(*b*) The A—H bond is not a —C—H bond, or any other type which will allow molecular oxygen to add onto it.

(*c*) The free radical A· decomposes to stable products.

Two types of molecular species fit these requirements well: aromatic amines and hindered phenols. In the case of the latter, for example, the free radical formed by the process:



is not likely to undergo the next step in the autoxidation process. The same considerations apply to aromatic amines. In order to increase the lability of the active proton, electron-repelling substituents are often introduced into suitable places in the aromatic ring.[6–8]

The types of molecule which exhibit antioxidant activity are therefore limited mainly (but by no means exclusively) to hindered phenols and aromatic amines. This fact is of importance to the analyst since it is one of the few factors which operates in his favour. However, the complex and variable fate of the radical A· is the source of considerable difficulty, since the products formed may fail to be identified.[9,10,11] The sample may therefore be contaminated with unknown amounts of unknown decomposition products, even though the antioxidant may have been separated from the polymer matrix and its associated free radicals.[1]

THE ANALYTICAL SCHEME

Analysis in situ

The difficulties involved in extraction of additives have resulted in a search for analytical techniques not involving prior separation of antioxidant from polymer. Of all those tried, only techniques based on spectroscopy can claim any degree of success. Ultraviolet examination of thin, hot-pressed polymer films has been tried by Luongo.[12] Using a double-beam spectrophotometer with air in the reference beam, he was able to estimate antioxidant levels ranging from 0·002 to 1·0% in polythene. However, such a procedure is limited by two factors: the polymer must exhibit a relatively flat absorption curve in the wavelength range used, and many antioxidants exhibit similar, if not identical ultraviolet spectra.

Miller and Willis[13] obtained infrared spectra of antioxidants from polymer films in a similar way, except that they compensated with additive-free polymer in the reference beam. Infrared is more specific than ultraviolet analysis, but some workers[14] find that the antioxidant level is too low to give suitable spectra. Drushel and Sommers find that they can combine specificity with sensitivity by using spectrofluorometric and phosphorescence techniques.[15] Again, they use a double-beam spectrophotometer, this time with a wedge of additive-free polymer in the reference beam. They admit, however, that the method is only applicable if the inhibitor has distinct, sharp bands, and no other components exhibit intense absorption in the same region.

"*In situ*" spectroscopic techniques are not likely to be of value, then, in the analysis of samples of unknown composition. If known amounts of antioxidant can be incorporated into additive-free polymer, however, these techniques are likely to be extremely useful in the study of extraction procedures, and the study of aging processes (including the effects of sterilizing radiation) since the rate of disappearance or of decay can be monitored directly by the decrease in absorbance of the sample at a suitable wavelength. Luongo, and Drushel and Sommers, have developed methods for putting known amounts of antioxidants into polymers. The former[12] prepares a master batch by milling a known amount of additive into his polymer and obtains standards by further milling uninhibited polymer with known amounts of master batch. He then hot-moulds his samples into films approximately 0·25 mm thick, either in a standard laboratory metallographic mounting press, or in a larger press between water-cooled, polished aluminium plattens. Drushel and Sommers[15] prepared their standards by adding the inhibitor in hexane solution to the polymer, evaporating the resulting slurry to dryness and hot-pressing between aluminium foil. In both cases, the films are mounted in frames before spectroscopic examination.

Analysis after separation

Separation of additives from polymer. In view of the limitations of "*in situ*" analysis, it seems inevitable that a preliminary separation of the antioxidant from the polymer will in most cases be necessary. Most of the many such separations which have been reported are concerned with solid/liquid extraction, since the insoluble nature of the polymer matrix precludes the possibility of using the more efficient liquid/liquid extraction. Much of the relevant information is summarized in Table I.

Table I.—Published methods of antioxidant extraction

Polymer type	Substances extracted	Extracting solvent	Comments	Refs.
Polythene	Cresols Phenolic antioxidants	Chloroform	Heat at 50° for 3 hr in closed container	16
Polythene	Cresols	Hexane	Heat at 50°	17
Polythene	Antioxidants	Ether	For 24 hr in the dark at room temperature	18
Polythene	Phenolic antioxidants	Chloroform		19
Polythene	Antioxidants	Toluene	Reflux to dissolve polymer and ppte with methanol	20 21,22 23
Polythene	Antioxidants	Water	At 70° under nitrogen	24
Polythene	Phenolic antioxidants	Compares carbon disulphide with isooctane	See text	25
Polyolefins	2,6-Di-t-butyl-*p*-cresol.	Cyclohexane	Reflux for 30 min	26
P V C.	Diphenyl thiourea 2-Phenylindole dicyandiamide	Methanol or ether		27
P V.C.	Stabilizers Lubricants Plasticizers	Ether		28
Rubbers	Amine and Phenolic Antioxidants	Ethanol/HCl	Reflux, then steam-distil amines from extract	29
Rubbers	Phenyl salicylate Resorcinol benzoate	Ether		30
Rubbers	Antioxidants	Acetone		31 32
Rubbers	Ketone-amine condensates Phenols 2-Mercaptobenzimidazole	Acetone		33
General	*p*-Phenylenediamine derivatives	95% Methanol or ethanol	For 16 hr in an extraction cup	34

One of the most difficult types of polymer to deal with, because of its insolubility, is the polyolefin variety. The British Standard method is favoured by some workers and involves dissolution of the polymer in boiling toluene under reflux followed by precipitation of the high molecular weight fraction with ethanol.[22,23] The filtrate then contains the additives plus an amount of low molecular weight polymer "wax" which usually requires painstaking removal.[1,17] Spell and Eddy, however, consider this procedure too time-consuming.[25] They have studied the extraction of the antioxidants Ionol (2,6-di-t-butyl-*p*-cresol) and Santanox [4,4′-thio-bis(6-t-butyl-*m*-cresol)] from polythene, and find that the required extraction time at room temperature varies linearly with polymer density and particle size, and the nature of the solvent. They conclude that if the polythene is powdered to 50-mesh, three hours' shaking in a wrist-action shaker is sufficient to recover 98% of either additive from polymer of any density. In support of these findings, some correlation has been found between the density of polythene and its permeability to solvents.[35,36] Other extraction apparatus described includes Soxhlet and related extractors,[1,34] tightly capped bottles in which sample and solvent are heated under pressure,[15] Wiley extractors,[26] and flasks in which the sample is merely steeped in solvent.[18] In order to increase the efficiency of extraction, surfactants and ultrasonic devices have been used.[37] Attempts to increase the polymer surface-area/weight-ratio before extraction have included the use of ball mills and Wiley cutting mills,[16,19,26] microtomes[38] and grinding with solid carbon dioxide.[27]

The Russian workers Yushkevichyute and Shlyapnikov describe an apparatus for the sublimation-distillation (*in vacuo*) of several antioxidants from polythene.[39] Using sublimation temperatures of 61–100° they were able to achieve satisfactory separation from polymers with molecular weights up to 50000. In a later publication[24] they report the extractive separation of certain antioxidants from polythenes with distilled water at 75° under nitrogen.

It must be concluded that apart from the work of Spell and Eddy, no thorough systematic investigation into the problems of quantitative extraction has been reported. No real attempts to minimize the decomposition and loss of sample during extraction seem to have been made, although such losses have been reported.[2,19] On the contrary, it seems probable that many of the recommended procedures involving prolonged heating would considerably speed up the rate of decomposition and oxidation unless stringent precautions are taken by use, for example, of inert-gas atmospheres. The technique of isotope dilution, which would avoid having to extract the inhibitor completely for quantitative analysis, has not been mentioned.

Separation of additives from each other. The separation of additives from each other after extraction from the polymer is necessitated by the lack of sufficiently specific methods for the identification of individual antioxidants in the presence of other components. In order to keep the analytical scheme as simple as possible, it would be desirable to eliminate this stage, but although one or two spot tests are described,[33–42] these are based on the formation of coloured products with various reagents, and are not specific enough to deal with the enormous number of antioxidants now commercially available. Most separatory techniques, however, also provide a clue to the identity of the components, and in a good scheme of analysis, the separatory process forms an important part of the actual identification procedure.

(*a*) *Liquid/liquid extraction.* Of all the well-known separatory techniques reported, liquid/liquid extraction seems to be the least frequently employed, although Brock and Louth[29] have devised an analytical scheme based almost entirely on it. Apart from this, it has been used mainly to separate antioxidants from soaps and inorganic stabilizers[28,43] and low molecular weight polymer fractions.[1]

(*b*) *Column chromatography.* Although column chromatography is probably the most exacting chromatographic technique to perform, it has the advantage of being able to deal with relatively large samples (50–5000 mg). Furthermore, the use of fraction collectors and automatic effluent-monitoring devices can make the method considerably easier to use. Fiorenza[44] separates antioxidants and plasticizers in rubber extracts by use of a neutral alumina column. He monitors the effluent with an LKB 254-nm ultraviolet-detector after eluting fractions successively with carbon tetrachloride, carbon tetrachloride/benzene mixture, benzene, benzene/ethanol mixture, and finally ethanol. Each separated component is identified by ultraviolet or infrared spectroscopy.

Crompton[1] recommends the use of a silica gel column on which the components of the polymer extract can be separated by use of a similar succession of increasingly polar eluents. He monitors the effluent with a JOEL JLC 2A recording chromatograph, which operates by measuring the thermal changes caused by components moving along the column. He points out that thin-layer chromatography can often be used as a short-cut to finding suitable adsorbents and mobile phases for column chromatography, since conditions experimentally found suitable for the former can usually be transferred without modification to the latter.

A synthetic rubber adsorbent is used by Berger *et al.*[45] to separate antioxidants. The stationary phase (Silastic 181) is applied to the column as a suspension in light petroleum and separation is carried out with a mobile phase of 21% v/v acetone in water. Cambell and Wise used an alumina column to separate phenolic antioxidants with chloroform followed by 10% v/v water in ethanol.[16] They used a Gilston Medical Electronics ultraviolet-scanner coupled to a recorder, to monitor the effluent stream.

An early separatory analytical scheme based on column chromatography was reported by Parker,[46] in which aliquots of the sample solution were chromatographed on seven alumina columns, each with a different mobile phase. From the position of the components on the various columns after a suitable elution time and from the colours obtained with specific detecting agents, he claimed to be able to obtain almost unambiguous identification of the antioxidants. Such a scheme would now be considered too wasteful and time-consuming to warrant consideration, but it paves the way for similar but more sophisticated techniques which follow.

(*c*) *Paper chromatography.* The advantages of paper over column chromatography are three-fold. It is simpler to use, smaller sample sizes can be used, and the R_F values are more reproducible, the last of these being particularly important since it permits identification of the separated components

Table II lists the more important paper chromatographic contributions in the literature.

Since most antioxidants are highly polar, they cannot be efficiently separated on normal paper except with the use of highly polar mobile phases. Consequently reversed-phase chromatography[49,50,54,56] or acetylated papers[31,55,59–61] are frequently employed to reduce the effect of "tailing" The detecting reagents used are either diazotized amines[53,55] which form coloured products with amines and phenols, or are oxidizing agents, since the oxidation products of antioxidants are generally highly coloured.[51,59–61] Sometimes the sample solution is treated with the colouring reagent first, and the coloured products are chromatographed[31,52,57] but multiple spots can be obtained from a single antioxidant treated in this way.[62]

A major contribution to paper chromatographic methods is the work of Zijp, who devised a comprehensive scheme for the systematic identification of antioxidants and accelerators.[59–61] In the part of his scheme which relates to antioxidants, Zijp used acetylated paper and two solvent systems, one for basic and one for phenolic constituents. Identification was based mainly on the R_F value of each constituent and the colours produced by various spray reagents. Auler, in his very full survey on the analysis of antioxidants and accelerators[62] was able to reproduce Zijp's work, and in addition, he applied the same solvent systems to circular paper chromatography with satisfactory results.

Williamson's important contribution[57] is based on that of Zijp, but employs different solvent systems. Before the chromatography, he evaporates the extract to dryness at 80° and takes up the residue in 96% ethanol. After the addition of three drops each of 20% strontium chloride solution and $4M$ ammonia, any impurities (mainly fatty acids) precipitate out and can be filtered off.

Unfortunately, the number of antioxidants now commercially available is so great that no single R_F value, even in conjunction with a variety of spray reagents, is likely to be specific enough to identify any component unambiguously. The analyst is therefore forced to consider the use of multiple solvent systems to achieve the specificity he requires, and at this point, paper chromatography becomes too lengthy a procedure for routine use. Consequently, later workers have turned to thin-layer chromatography.

(*d*) *Thin-layer chromatography.* Thin-layer chromatography is a much more rapid technique than paper chromatography and also allows more corrosive spray reagents to be used. Unfortunately, however, the reproducibility of R_F values is generally poorer than in paper chromatography.[48] Nevertheless, recent papers by Dallas[63] and other workers[64,65] have indicated that reproducibility can be improved if full account of all the experimental variables is taken.

Probably the most important contribution based on TLC is that of van der Neut and Maagdenderg.[74] In their scheme, the first chromatogram separates the antioxidants into groups according to R_F ranges. Based on this preliminary classification, a second solvent system is selected and then, if necessary, a third and fourth until complete identification is achieved. In all, nine solvent systems are specified together with four detecting reagents. The scheme is comparable to the scheme devised for the identification of metals *via* groups, and has been applied, with success, to over thirty antioxidants. Newly applied antioxidants can be easily inserted into the scheme. However, the success of this system depends to a large extent on the reproducibility of the R_F values obtained, and the authors do not, unfortunately, give any account of their experimental procedure.

In contrast, Crompton[1] gives an excellent account of experimental TLC of polymer additives. He applies a 1% solution of polymer extract as a continuous band along the bottom of two 20 × 20 cm plates one of which is made up from silica gel G 254, and the other from silica gel GF 254 (Merck) which contains a

TABLE II.—SEPARATION OF ADDITIVES–PAPER CHROMATOGRAPHIC METHODS

Substances separated	Stationary phase	Mobile phase	Derivative or treatment	Detection	Comments	Refs
Gallates Gallic acid Butylated hydroxyanisole	7% liquid paraffin on paper	Light petroleum		Ammoniacal silver nitrate	Descending run–4 hr	49 50
Antioxidants in food and fats	Paper	Acetic acid–water (1:4)		0·2% $Fe_2(SO_4)_3$–0 1% $K_3Fe(CN)_6$ (1 1)	Blue spots	51
Amine antioxidants	Paper	Acetic acid–water–acetone (3.6.1)	React with 3-methylbenzothiazolin-2-one hydrazone HCl/$FeCl_3$ before chromatography	Products coloured		52
Antioxidants	Paper	Not given	Heated under reflux with HCl	Sulphanilic acid–sodium nitrite or ninhydrin		53
Aromatic amines and phenothiazine antioxidants	Dipropylene glycol (I) on paper.	Cyclohexane saturated with I		UV light or *p*-Nitrobenzenediazonium fluoroborate	112 μg detected	54
Antioxidants	Whatman acetylated paper No AC82	Ethanol–benzene–acetylacetone (10 10.1)	Antioxidants extracted from accelerators with ethanol	Potassium *p*-diazobenzene sulphonate	Ascending against the grain–5 hr	5
Antioxidants	Acetylated Whatman No. 1	Not reported	Extract into ethanol add 4*M* NH_4OH, 20% $SrCl_2$ and filter			31
Catechols	Whatman No. 1 impregnated with formamide + H_3PO_4, dimethylformamide or liquid paraffin.	(*a*) Isopropyl-ether (*b*) Chloroform (*c*) Heptane (*d*) Heptane–benzene (1:1) (*e*) 80% Methanol				56
Antioxidants and accelerators	Paper		Coupled with *p*-diazobenzene sulphonic acid, or alkali	Products coloured		57
Urea-based stabilizers	Paper	Propanol–methanol–water (2:1:1)		*p*-Dimethylaminebenzaldehyde		27

Antioxidants	Paper	Chloroform–acetic acid (99 1)		Ascending technique in atmosphere from 50% acetic acid	58
Basic antioxidants	Acetylated Whatman No. 1	96% Ethanol–benzene (1 1)	4% Benzoyl peroxide in benzene		59 60 61
Phenolic antioxidants	Acetylated Whatman No. 1	Butyl acetate–pyridine–methanol–water (1:5·1:3)	Tollens' reagent, Millon's reagent.		
Basic antioxidants	Schleicher and Schull 2043b/45ac	96% Ethanol–benzene (1.1)	1% Diazobenzene sulphonic acid (DBS) in 25% aqueous acetic acid, or 20 mg of DBS in 5 ml of 0 1*M* NaOH + 5 ml of 96% ethanol		62
Phenolic antioxidants	Schleicher and Schull 2043b/45ac	Butyl acetate–pyridine–Methanol–water (1:5 1·3)	Tollens' reagent, Millon's reagent, phosphomolybdic acid, vanillin or potassium ferricyanide		

TABLE III.—SEPARATION OF ANTIOXIDANTS—THIN-LAYER CHROMATOGRAPHIC METHODS

Substances separated	Stationary phase	Mobile phase	Detection	Refs.
Phenolic antioxidants	Silica gel G	Methanol–cyclohexane (1.24)	30% Molybdophosphoric acid + ammonia vapour	17
Organo-tin stabilizers	Not stated	Acetic acid–isopropyl ether (1 5.98 5)	20% Molybdophosphoric acid + ammonia vapour	66
Antioxidants	Not stated	Light petroleum–ethyl acetate (9.1)	(*a*) Ethanolic 2,6-dichloro-*p*-benzoquinone-4-chloramine + 2% aq. $Na_2B_4O_7$ (b) Diazotized *p*-nitroaniline	18
Organic stabilizers	Kieselgel G	Ethanol-free chloroform		67
Phenolic antioxidants	Polyamide powder	Methanol–water (3:2) or Methanol–carbon tetrachloride (1·9)	Diazotized sulphanilic acid	68
Phenyl salicylate Resorcinol benzoate	Kieselgel G	Dichloromethane or isopropyl ether–light petroleum (40–60°) (7:3)	UV Light	30
BHA, 2,6-di-t-butyl-*p*-cresol	Silica gel	Chloroform	20% Molybdophosphoric acid + ammonia vapour	69
Antioxidants	Polyamide powder	Methanol–acetone–water (6.1 3)	Diazotized sulphanilic acid or molybdophosphoric acid	70
Antioxidants	Kieselgel G		α,α′-Diphenyl-β-picryl hydrazyl (free radical)	21
Antioxidants	Alumina + 5% Plaster of Paris on microscope slide	Petrol–dioxane (10·1)	5% Ethanol, phosphomolybdic acid	11
Antioxidants	Silica gel	Acetone, chloroform, benzene, carbon tetrachloride or binary mixtures		32
Antioxidants	(*a*) 10% Starch in polyamide powder (*b*) 10% PVC in polyamide	Methanol–acetone–water (3 1.1) light petroleum–benzene–acetic acid–DMF (40.40.20 1)		72
Antioxidants	Silica gel G	Benzene	0·05% $Fe_2(SO_4)_3$ in sulphuric acid + 0 2% $K_4Fe(CN)_6$ (1:1)	73
Polymer additives	Silica gel	Light petroleum (40–60°)–ethyl acetate (9 1)	See Table V	1
Antioxidants	Not stated	See text	See text	74

fluorescent indicator. After development, the plates are examined under 254 or 366 nm radiation so that any substances on the plates which absorb radiation at a wavelength above 230 nm appear on the fluorescent silica gel as dark areas on a blue fluorescent background. Any substances which themselves fluoresce appear on the non-fluorescent plate. After the positions of the substances so revealed have been marked, the plates are sprayed with aggressive spray reagents (Table IV) to reveal any additional components. Further identification is achieved by spraying additional plates with more specific reagents and by simultaneously running known antioxidants on the chromatogram. The author points out that many commercially available grades of silica gel contain traces of organic impurities which interfere by reacting with the spray reagent or by absorbing in the ultraviolet or infrared when isolated components are separated from the plate and subjected to spectroscopy for further identification. These effects can be avoided, however, by first developing the plate in a highly polar solvent which pushes the impurities to the solvent front. The plate can then be redried and used for the analysis of polymer extract.

TABLE IV.—GENERAL SPRAY REAGENTS FOR LOCATION OF COMPOUNDS ON SILICA GEL COATED PLATES

Reagents applied to GF 254 plate without subsequent heating	
Potassium permangate (0·1N) in aqueous sodium carbonate (5% w/v)	
Potassium permanganate (2% w/v) in aqueous sulphuric acid (6% v/v)	
Potassium permanganate (0·1% w/v) in sulphuric acid (96%)	
Antimony pentachloride (20% w/v) in carbon tetrachloride	
Phosphomolybdic acid (3% w/v) in ethanol, then plate exposed to ammonia vapour	
Reagents applied to G 254 plate with subsequent heating	
	Heat treatment
Sulphuric acid aqueous (20% w/v)	5–15 min at 120°C then 5 min at 150°C
Potassium permanganate	(2% w/v) in aqueous sulphuric acid (6% v/v)
Phosphoric acid (10%) in methanol	
Perchloric acid (2%) in methanol	
Antimony pentachloride	(20% w/v) in carbon tetrachloride
Phosphomolybdic acid (20% w/v) in methanol or methyl cellosolve	5–15 min at 120°C

(*e*) *Gas-liquid chromatography* (*GLC*). The enormous amount of GLC data which has been published over the last few years contains many references to the separation of phenols and amines. Some of the work which is more directly applicable to the analysis of antioxidants is listed in Table V.

The attraction of GLC lies in its ability to simultaneously separate, identify and estimate sub-milligram quantities of complex mixtures, and it would therefore seem to be the complete answer to the problems so far outlined. There are, however, serious drawbacks to the method. Retention times are no more specific for GLC than are R_F values for thin-layer or paper chromatography. Day-to-day reproducibility is not good for most instruments running at high temperatures and varies considerably with the condition of the column. Since many antioxidants are not volatile, low stationary-phase loadings have to be used in order to cut retention times to a sensible value, which means that large areas of uncoated solid support appear which in turn lead to bonding by phenols and amines to the column, resulting in the distortion of peaks and lengthening of retention times. There are, however,

TABLE V.—SEPARATION OF ANTIOXIDANTS—GAS LIQUID CHROMATOGRAPHIC TECHNIQUES

Substances separated	Stationary phase	Column temp. °C	Other details	Refs.
2,6-Di-t-butyl-*p*-cresol, 2-(2-Hydroxy-5-methylphenyl) benzotriazole	25% LAC-2R/446 (adipate ester) + 2% H_3PO_4 on chromosorb	135	H_2 carrier gas, F.I.D. Error ± 1%	75
2,6-Di-t-butyl-*p*-cresol, (I) 2,6-Di-t-butyl phenol 2,4,6-tri-t-butyl phenol Diphenylamine	10% Apiezon N on celite 545	164	H_2 carrier, F.I.D. 10^{-8} *M* I in presence of others can be detected	76
2,6-Di-t-butyl-*p*-cresol Phenyl-2-naphthylamine	Apiezon		F I D.	77
Halogenated bisphenols	10% DC-710 Silicone oil on chromoport xxx 80–100 mesh	225–250	12-in. glass column, ¼ in o d Carrier: 130 ml He/min	78
Low b.p. phenols	Capillary column coated with 10% xylenol phosphate	125	F.I.D.	79
Amine antioxidants	20% Apiezon L on 30–60 mesh chromosorb W.	300	2-metre, ¼ in. o d. column	80
Phenol and 5-t-butyl derivatives	Silicone oil 550–carbowax 400 (3:2)	200	Mean deviation 0 4%	81
Phenols and cresols	5% w/w of various phosphate esters of phenols	110	120 cm × 4 5 mm column, Pye-Argon Chromatograph	82
Ionox 330 (see text)	(*a*) 20% DC-710 Silicone oil on chromosorb.	200–300 in 10 min	(*a*) 12 × 3/16 in. column	83
	(*b*) 2% SE.30 silicone gum on chromosorb mesh		(*b*) 12 × 1/16 in. stainless-steel column	
Low molecular weight phenols	Silicone-coated capillary column		Converted to trimethylsilyl esters before chromatography.	84
2,6-Di-4-methylphenol	20% SE.30 on HMDS-treated 60 mesh chromosorb W	200	E C. detector	85
Ionox 330	5% SE 30 on 80–90 Anakrom absorbant	290	He-Carrier	1

HMDS = hexamethyldisilazane
E.C = electron capture
F.I D. = flame ionization detector.

measures which can be taken to meet these difficulties. For example, relative retention times are often more reproducible than unadjusted retention times, non-volatile components can be converted into more volatile derivatives such as trimethylsilyl ethers[84] which also help reduce bonding to the column. The solid support can also be treated (for example, with hexamethyldisilazane) to reduce the number of active sites on the column available for bonding.[85] With the use of high temperatures or temperature programming coupled with high carrier gas flow-rates and low stationary-phase loadings, it may be possible to chromatograph relatively high molecular weight substances. Knight and Seigel[83] and Crompton[1] have been able to chromatograph the antioxidant Ionox 330 (1,3,5-trimethyl-2,4,6-tri(3,5-di-t-butyl-4-hydroxybenzyl)benzene, which has a molecular weight of 775 (vapour pressure 0·014 mm at 180°) with a retention time of less than 10 min. It must be pointed out, however, that the formation of derivatives before chromatography almost invariably leads to some sample loss and can often result in the appearance of spurious peaks. Furthermore, instrumental parameters on most instruments cannot be varied far from the optimum. Finally, the lack of specificity can only be overcome by using a variety of columns in the manner described for paper and thin-layer chromatography. Column changing is a tedious and inconvenient procedure and the cost of spare columns is prohibitively high.

It must be concluded, therefore, that although GLC will play its part in the analytical scheme, it is not likely to replace TLC as the basis for it at the present time. The possibility of using pyrolysis gas chromatography is now being considered;[14] this may eventually change the situation.

(*f*) *Electrophoresis.* This separatory technique does not seem to have received much attention by antioxidant analysts. A Japanese paper[86] reports on successful separations by coupling the antioxidants with *p*-diazobenzenesulphonic acid before electrophoresis. Amines are coupled in acetic acid, and phenols in sodium hydroxide–ethanol. Electrophoresis is carried out in 1% w/v methanolic sodium borate.

No reference to thin-layer electrophoresis was found.

Identification of separated antioxidants

The identification of antioxidants by means of R_F values and spray reagents has been described in some detail, but although this technique may suffice in the majority of cases, it must be remembered that this is identification by inference, and occasionally a more positive identification may be required. It may sometimes happen, for example, that an R_F value does not correspond to a previously tabulated value, or it is suspected that the unknown component is not an antioxidant, but some other type of additive. Alternatively, the situation may arise in which no separatory procedure is required, and lengthy chromatographic analysis can be avoided by a more direct method of identification. The following is a classification of identification techniques which have been used.

Ultraviolet and visible spectroscopy. Ultraviolet spectroscopy is not a good tool for the identification of unknown constituents since it is non-specific and subject to many interferences. Nevertheless, ultraviolet spectra obtained from polymer extracts continue to be published.[38,44,53,87] Sircar *et al.*[40] were able to distinguish between various *p*-phenylenediamine-type antioxidants by means of the colours produced with acid permanganate in ethanol (which they measured spectroscopically), but only a few of such compounds were studied. Hilton also adopted a colorimetric technique for the identification of amines.[88,89] He extracted them with ethanol and coupled them with diazotized *p*-nitroaniline. Kabota *et al.*[90] made coloured derivatives of amines with benzothiazolin-2-one hydrazone hydrochloride and iron(III) chloride before spectroscopy.

Interferences in direct ultraviolet spectroscopy have been minimized by selective extraction[24,29,46] or chromatography.[44] The use of ultraviolet light in monitoring chromatographic effluents has previously been noted, as has its use in the examination of thin polymer films without separation of the antioxidant. Qualitative ultraviolet spectroscopy is also mentioned in various reviews.[46,62,92]

Infrared spectroscopy. Infrared spectra give much more information than ultraviolet spectra and are less subject to interference from small amounts of impurity. Their main disadvantages are that comparatively large amounts of sample are normally required, and that the spectra are too detailed to be useful for complex mixtures.

Nevertheless, some workers find that infrared examination of polymer extract without further separation can yield useful information.[28,53,91–93] Often, however, such examinations are carried out after the isolation of individual components. Crompton, for example, scrapes separated components from the TLC plate, elutes them from adsorbent, and studies them by infrared in a potassium bromide disc.[1] He publishes the spectra of Ionol (2,6-di-t-butyl-*p*-cresol) and its degradation products which he isolated from polythene in this way. McCoy[94] has developed a technique for obtaining infrared spectra from 50–100 μg of component on a TLC plate by elution with a solvent into an infrared cavity-microcell. He illustrates this technique with a spectrum of Ionox 333 so obtained. Fiorenza[47] uses column chromatography to simplify his polymer extract before using infrared.

Finally, Hummel has published a comprehensive table giving infrared data on all polymer additives.[95]

Fluorometric and phosphorescence analysis. Aromatic amines and phenols are among the few classes of compounds in which a large proportion of the members exhibit sensible fluorescence. Apart from this specificity, fluorescence techniques are far more sensitive than absorption spectroscopic techniques, and it is, therefore, surprising that more use has not been made of fluorimetry in the analysis of antioxidants. Parker and Barns[96] for example find that in extracts from rubbers the strong absorption by pine-tar and other constituents masks the absorption spectra of phenyl-naphthylamines, whereas their fluorescence spectra are sufficiently unaffected for them to be determined directly in the unmodified extract by this method. In a later paper[97] Parker also discussed the possibility of using phosphorescence techniques for determining these compounds.

The use of spectrofluorimetry in the study of thin polymer films has already been discussed

Other techniques. Mass spectrometry has been used to identify Ionol in polythene.[98] Amines have recently been studied by this technique [99,100] One publication[29] also mentions the use of X-ray diffraction in antioxidant analysis.

Quantitative analysis

The final step in the analytical scheme is the estimation of the amount of identified antioxidant in the original material. This information may not always be required, but when it is, the problem of quantitative extraction from the polymer is likely to be the factor which sets a limit on the accuracy of the results obtained. Because of the reactivity of antioxidants, there is no lack of methods for their quantitative estimation once they have been isolated.

Spectroscopic methods. By far the most popular method of estimating antioxidants is by coupling or oxidizing them to form coloured products and measuring the resulting absorbance in the visible region of the spectrum. This technique is not particularly specific for individual antioxidants, but it is specific for amines and phenols if the correct reagents are used and hence small amounts of impurities from other additives do not interfere. Table VI lists a number of such methods which have been reported.

TABLE VI— COLORIMETRIC ANALYSIS OF ANTIOXIDANTS

Substances estimated	Colour reaction	Refs.
2,6-Di-t-butyl-*p*-cresol	Extract into cyclohexane and oxidize in KOH-saturated isopropanol	26
Antioxidants (general method)	Couple with α,α'-diphenyl-β-picrylhydrazyl (measure decrease of absorbance)	101
Amines	(*a*) Couple with *p*-diazobenzenesulphonic acid (*b*) React with benzoyl peroxide	86
Butylated hydroxytoluene (BHT)	React with 2,6-dichloro-*p*-benzoquinone-4-chloramine	103
p-Phenylenediamine derivatives	Ethanol extracts coloured by reaction with cupric acetate in KCl/HCl buffer	34
N,N'-di-2-naphthyl-*p*-phenylenediamine	Oxidize with H_2O_2/H_2SO_4	23
Phenolic antioxidants	Diazotized sulphanilic acid	22
Amine antioxidants	Diazotized *p*-nitroaniline	88
BHT	Dissolve in KOH–80% ethanol	45
Antioxidants (general method)	Extract with toluene–ethanol and treat with $FeCl_3$. Measure resulting $FeCl_2$ with 2,2'-dipyridyl	20

This non-specificity also provides a means of estimating total antioxidant content if no identification is required. Glavind[101] and Blois,[102] for example, measure total antioxidants by combining them with the free radical α,α-diphenyl-β-picrylhydrazyl. A British Standard method for measuring total phenolic antioxidants involves coupling them with diazotized sulphanilic acid.[22] Metcalf and Tomlinson have developed a general method in which the antioxidants are first treated with iron(III) chloride, and the resulting iron(II) is estimated colorimetrically with the 2,2'-dipyridyl [20]

Straightforward ultraviolet spectroscopy is liable to be in error owing to highly absorbing impurities in the sample. In an attempt to overcome this difficulty, however, Wexler[104] makes use of the bathochromic shift exhibited by phenols on changing from a neutral or acidic medium to an alkaline one; this is due to the change of absorbing species because of solute–solvent interaction. Wexler, using a double beam recording spectrophotometer, measured a difference spectrum by placing an alkaline solution of the sample in the sample beam, and an identical concentration of sample in acid solution in the reference beam. In this way he was able to obtain quantitative information about thirteen phenols, free from interference.

Scheele and his co-workers[105,106] have found extensive agreement between conductimetric and ultraviolet spectroscopic methods of quantitative antioxidant analysis.

An interesting Russian paper[107] reports that inhibitors of free radical oxidation also cause a decrease of fluorescence under certain circumstances, and that this effect could be used to determine the reaction rate or the concentration of the inhibitor present.

Phenoxy free radicals have been determined by electron spin resonance[108] but this technique is of little use for actual antioxidant analysis.

Titrimetric methods. Numerous titrimetric methods have been developed for the assay of small amounts (1–200 mg) of antioxidants. Davis[109] was able to estimate 1–20 mg of a *p*-phenylenediamine derivative by visual titration in chloroform with toluene-*p*-sulphonic acid, Methyl Orange being used as indicator. The same type of antioxidant is oxidized with chloranil to form one equivalent of base by Lorenz and Parks.[41] The base is then titrated in non-aqueous medium with perchloric acid. A Japanese paper[110] extends the non-aqueous technique to phenols by titrating in pyridine with sodium isopropoxide; the end-point is detected potentiometrically or conductimetrically. Schröder and Rudolph[19] determine phenolic antioxidants by treating the polymer extract with potassium bromide–bromate and estimating the unconsumed bromide with thiosulphate. This can be done with less than 1 mg of sample.

Hydroquinone, which is sometimes used as an antioxidant, has been estimated by titration with *N*-bromosuccinimide, with starch–iodide to detect the end-point.[111]

Several complexometric methods are reported, based on the reduction by antioxidants of silver nitrate to metallic silver.[58,112,113] The precipitated silver is re-dissolved and titrated with EDTA *via* the substitution reaction with tetracyanonickelate.[114]

Finally, an ingenious use of 2,4,6-tri-t-butylphenoxy radicals is reported by Paris *et al.*[115] This reagent reacts with atomic oxygen and various antioxidants with stoichiometry dependent upon the number of labile hydrogen atoms they contain. Titrations can be monitored potentiometrically or spectrophotometrically at 625 nm.

Electrochemical techniques. The use of polarography in the analysis of polymer additives has been extensively studied by Mocker,[116–118] and Mocker and Old,[119] who find the technique more applicable to accelerators than to antioxidants. Difficulties arise because the dropping mercury electrode (DME) cannot be used at potentials more positive than +0·4 V with respect to the saturated calomel electrode, and since many aromatic amines and phenols can only be oxidized at electrodes, positive voltages have to be applied in their analysis. Nevertheless, the polarography of some amines and phenols has been studied[120–123] and whilst no electrode is as suitable for polarography as the DME, antioxidants have also been studied with other electrodes, notably the graphite[124,125] and platinum[126] electrodes. The related technique chronopotentiometry has also been used with a graphite electrode for the study of antioxidants[127] but although these procedures have been moderately successful the time and care needed to achieve reproducible results do not warrant using them when simpler techniques are available.

In addition, at least two commercially available antioxidants have been shown by differential cathode-ray polarography to exhibit reduction waves: Santanox [4,4′-thiobis-(3-methyl-6-t-butylphenol)] gives a poorly shaped wave at —0·6 V in an electrolyte consisting of ammonia and ammonium chloride in methanol–water,[128] and 3,5-di-t-butyl-4-hydroxytoluene gives a wave at —0·65 V in aqueous sodium or lithium hydroxide.[129] In both cases, 40 ppm of analyte gave a current which was adequate for quantitative analysis.

Other papers mention the conversion of an antioxidant into a polarographically reducible form[130] and a general method for antioxidants which involved measuring a decrease in the height of the wave, due to the reduction of dissolved oxygen by antioxidants.[131]

Amines and phenols have also been titrated electrometrically with lithium aluminium hydride, with platinum or silver electrodes,[132] but, not surprisingly, small amounts of water affect the accuracy of the results.

Gas liquid chromatography. Conditions under which antioxidants have been successfully subjected to gas chromatography have already been reviewed above. It is sufficient now to note that results with an error of not more than ±2% should be easily obtainable by the internal marker technique.

DISCUSSION AND CONCLUSION

It is apparent that a lack of sufficiently specific analytical techniques makes the separation of antioxidant first from the polymer and then from other additives necessary prerequisites to any comprehensive scheme of analysis. The first of these separatory steps does not seem to have been studied as fully as might be expected, especially with regard to sample degradation. Useful indications of how this might be achieved are given by the *in situ* techniques of Luongo[12] and Drushel and Sommers.[15]

The second step is clearly attainable by chromatography, since isolation and identification can then be done simultaneously, although it is evident that with the variety of antioxidants now available, no simple chromatographic identification will be adequate. The most promising approach seems to be that of van der Neut and Maagdenberg[74] in which the sample is developed in a series of solvents according to its R_F value in each preceding system. Because of its speed and comparative cheapness, thin-layer chromatography seems most readily applicable to such a scheme, provided that R_F values can be made reproducible in the manner, for example, of Dallas.[63]

There is no shortage of techniques for the final quantitative determination of the isolated antioxidant because of its inherent reactivity.

If such a scheme as outlined above appears unduly lengthy, it must be remembered that in most cases the analyst has prior knowledge concerning the sample, or only requires limited information from his analysis, so that identification can be simplified to perhaps one or two chromatograms containing the sample plus standard aliquots of the materials suspected to be present. This in no way invalidates the usefulness of a general comprehensive scheme for the identification of unknowns (which incidentally, can be applied equally well in the most part to other commodities containing antioxidants, such as foodstuffs and lubricating oils). Moreover, such a scheme, by allowing the inclusion of new antioxidants as and when they are developed, would meet the future needs of this expanding sphere of technology for some time to to come.

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Zusammenfassung—Eine Ubersicht uber Methoden, die zur Analyse von Antioxidantien in Polymeren vorgeschlagen werden, in Form einer stufenweisen Untersuchung der Probleme, die in jedem Analysenschema enthalten sind, mit einer kritischen Würdigung der publizierten Vorschriften zu ihrer Überwindung.

Résumé—Une revue des méthodes proposées pour l'analyse des antioxydants dans les produits polymères, donnée sous la forme d'un examen point par point des problèmes liés à n'importe quel schéma d'analyse, avec une appréciation critique des techniques publiées conçues pour les surmonter.

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MIXING EFFICIENCY AND INSTRUMENTAL DELAY EFFECT ON RECORDED KINETIC CURVES

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Summary—The effect of reactant addition time and instrumental response time on recorded kinetic curves was considered. The mixing-time effect was considered for first- and second-order reactions in the case that a simple function of the concentration is measured, and for first-order reactions in the more complex case of non-adiabatic enthalpimetric measurements. For any ratio of addition time to half-transformation time the proposed equations allow calculation of the correct rate constant and the error in the calculated initial concentration extrapolated from the experimental curve and show which portion of the experimental curve must be disregarded owing to the misleading effect of the addition time. The distortion due to the response-time of a thermistor used as concentration transducer has been calculated from a simplified model. The experimental kinetic measurements performed by quasi- and non-adiabatic enthalpimetry agree very satisfactorily with the theoretical data.

IN FAST and moderately fast chemical kinetics, the accuracy of measurement of the physical quantity used to follow the concentration (c) of one component of the system as a function of time (t), depends mainly on two factors: the instrumental response and the time taken to add one reactant to the other (addition time). The faster the reaction, the more significant will be the distortion of the experimental $f(c)$ *vs.* t curve. On the other hand the more complete the mechanistic study on chemical kinetics, the larger the variation of reactant concentration required, and hence the possibility of having to follow a fast reaction.

The effect of addition time on the value of a first-order rate constant has been calculated, as far as we know, only for flow-methods, by Caldin and Trowse.[1] It was therefore interesting to find general relationships for predicting the errors due to addition time and instrumental time-lag on the experimental $f(c)$ *vs.* t curve.

In the present paper the addition time effect for different ratios $t_{1/2}/t_A$ ($t_{1/2}$ = half-transformation time, t_A = addition time) has been calculated for first- and second-order reactions in which one reactant is added to a fixed volume of the other, and so has the effect due to the response time of the temperature-measuring device in quasi- and non-adiabatic enthalpimetric measurements.

For simplicity it was assumed that the reactant is added at a constant rate and the solutions are mixed sufficiently quickly to ensure instantaneous homogeneity, and that the volume change can be neglected.

In the experimental work, however, we found that the addition time can be lowered to 0·1 sec but the complete mixing time cannot be lowered to less than 1 sec, and furthermore, an addition time of about 1 sec or more is equivalent to the total mixing time.

ADDITION-TIME EFFECT

First-order reaction

Let t_A be the time needed to add n_0 mole of reactant R. At time t the amount added will be $n_t = n_0 t/t_A$, and if n is the number of moles that have reacted,

$$\frac{dn}{dt} = k_1(n_t - n) = k_1 n_0 \frac{t}{t_A} - k_1 n \tag{1}$$

Integration of equation (1) gives: for $t \leqslant t_A$

$$n_{t \leqslant t_A} = e^{-k_1 t}\left(C + \int \frac{k_1 n_0 t}{t_A} e^{-k_1 t}\, dt\right) = \frac{n_0}{k_1 t_A}\left(e^{-k_1 t} + k_1 t - 1\right). \tag{2}$$

where C is an integration constant which can be calculated from the initial conditions. For $t > t_A$ the reaction will proceed as a normal first-order reaction, the initial quantity of R being

$$n_0(1 - e^{-k_1 t_A})/k_1 t_A$$

and the quantity which has reacted being

$$n_{t > t_A} = \frac{n_0}{k_1 t_A}\left[(1 - e^{-k_1 t_A})(1 - e^{-k_1(t - t_A)}) + (e^{-k_1 t_A} + k_1 t_A - 1)\right]$$

$$= n_0\left[1 - \frac{1}{k_1 t_A}(1 - e^{-k_1 t_A})e^{-k_1(t - t_A)}\right]. \tag{3}$$

For all experimental methods, such as quasi-adiabatic enthalpimetry, where the measured physical quantity h is a linear function of the number of moles reacted,

$$h_{t \leqslant t_A} = \frac{h_0}{t_A}\left[t - \frac{1}{k_1}(1 - e^{-k_1 t})\right] \tag{4}$$

and

$$h_{t \geqslant t_A} = h_0 - \frac{h_0}{k_1 t_A}(1 - e^{-k_1 t_A})(e^{-k_1(t - t_A)}) = h_0 - \frac{h_0}{k_1 t_A}(e^{k_1 t_A} - 1)e^{-k_1 t} \tag{5}$$

where $h_0 = h$ for $t \rightarrow \infty$.

Relating the addition-time t_A to $t_{1/2}$ by $t_A = x\, t_{1/2} = 0{\cdot}693x/k_1$, one can write equations (4) and (5) in the more general form:

$$h^*_{t \leqslant t_A} = h_0\left[1 - \frac{t}{x t_{1/2}} + \frac{1}{0{\cdot}693x}(1 - e^{-0{\cdot}693t/t_{1/2}})\right] \tag{4'}$$

$$h^*_{t \geqslant t_A} = \frac{h_0}{0{\cdot}693x}(e^{0{\cdot}693x} - 1)e^{-0{\cdot}693t/t_{1/2}} \tag{5'}$$

where $h^* = h_0 - h$ is proportional to the number of moles $n_A - n$ unreacted.

From equations (4′) and (5′) it follows that the experimental curve can be treated as a normal first-order reaction after t_A, but during the interval from $t = 0$ to $t = t_A$ the amount of reactant will have diminished to $n_0 h_{t_A}/h_0$ *i.e.*, $n_0(1 - e^{-0{\cdot}693x})/0{\cdot}693x$, which is only about 70% of n_0 if $t_A = t_{1/2}$, for example.

This means that, as the addition time cannot be generally lowered to less than 1 sec, only reactions with half-time of the same order can be followed.

If extrapolation to $t = 0$ is carried out, as in the determination of n_0 in a mixture by differential kinetic measurements, equation (5′) shows that the normal procedure will yield not h_0 but $h_0(e^{0\cdot693x} - 1)/0\cdot693x$.

Effect on non-adiabatic enthalpimetric measurements. This case is particularly interesting since it is claimed that chemicals kinetics with $t_{1/2}$ down to 0·2 sec can be studied.

Remembering[2] that the temperature change is related to the number of moles reacted by:

$$\frac{dn}{dt}\frac{\Delta H}{c} = \frac{dT}{dt} + k_2\Delta T \tag{6}$$

where ΔH = molar enthalpy of reaction, k_2 = the Newtonian first-order heat-exchange constant, and the other symbols have the usual meaning, then at $t < t_A$, from equation (2),

$$\frac{dn}{dt} = n_0\,\frac{1 - e^{-k_1t}}{t_A}. \tag{7}$$

From equation (6):

$$\frac{\Delta H}{c}\frac{n_0}{t_A}(1 - e^{-k_1t}) = \frac{\Delta T_0}{t_A}(1 - e^{-k_1t}) = \frac{dT}{dt} + k_2\Delta T \tag{8}$$

where ΔT_0 is the maximum temperature change corresponding to adiabatic conditions.

Integration of equation (8) with $\Delta T = 0$ at $t = 0$ gives

$$\Delta T_{t<t_A} = \frac{\Delta T_0}{k_2t_A}\left(1 + \frac{e^{-k_1t}k_2}{k_1 - k_2} - \frac{k_1e^{-k_2t}}{k_1 - k_2}\right). \tag{9}$$

Analogously from equation (3), at $t > t_A$

$$\frac{dn}{dt} = \frac{n_0}{t_A}(1 - e^{-k_1t_A})e^{-k_1(t-t_A)}. \tag{10}$$

The integration of equation (6) with ΔT_{t_A} obtained from equation (9) gives

$$\Delta T_{t>t_A} = \frac{\Delta T_0}{t_A(k_2 - k_1)}\left[\frac{k_1}{k_2}(1 - e^{k_2t_A})e^{-k_2t} + (e^{k_1t_A} - 1)e^{-k_1t}\right]. \tag{11}$$

The first derivative with respect to t gives a maximum at

$$t_{\max} = \frac{2\cdot3}{k_1 - k_2}\log\frac{e^{k_1t_A} - 1}{e^{k_2t_A} - 1} \tag{12}$$

which corresponds to:

$$\Delta T_{\max} = \left[\frac{e^{k_1t_A} - 1}{e^{k_2t_A} - 1}\right]^{k_1/k_2-k_1}\cdot\frac{e^{k_1t_A} - 1}{k_2t_A}\Delta T_0 \tag{13}$$

The limit of equation (13) with $t_A \to 0$ is the usual expression[2]

$$\Delta T_{\max} = \Delta T_0 \left(\frac{k_1}{k_2}\right)^{k_2/k_2-k_1} \tag{14}$$

Equations (12) and (13) allow calculation of the addition-time effect on the position of the maximum on the curve of ΔT *vs.* t. A non-instantaneous addition will cause a lowering of $\Delta T_{\max}$ and a shift of the curve and of $t_{\max}$ towards higher values of t. The extent of these effects depends on both x and $t_{1/2}$. For example, for two different values of $t_{1/2}$ and the same value of x one has:

$t_{1/2}$, *sec*	t_A, *sec*	x	$\dfrac{t_{\max}}{(t_{\max})_{x=0}}$	k/k_{app}	k_2
1·8	1·8	1	1·14	1·20	0·03
0·2	0·2	1	1·08	1·10	0·03

The experimental k value will appear 10% less than the theoretical if an addition time of 0·2 sec is assumed, but since complete mixing generally requires about 1 sec, an error of about 60% in the value of k must be expected. With a higher value of k_2, the error will increase further.

Second-order reaction

Starting from a second-order reaction equation

$$\frac{dn}{dt} = k_1(a - n)(b - n) \tag{15}$$

(where a moles of one reactant are added to b moles in one liter of solution of the other), at $t \leqslant t_A$ we have

$$a = n_A t/t_A$$

where n_A is the total number of moles added at t_A, and so

$$\frac{dn}{dt} - k_1 n^2 + \frac{k_1 n n_A t}{t_A} + k_1 bn - \frac{k_1 b n_A t}{t_A} = 0 \tag{16}$$

Equation (16) is of the Riccati type. The solution of this equation gives:

$$n_{(t \leqslant t_A)} = \frac{c_1 b\left[\sqrt{\dfrac{\pi n_A k_1}{2t_A}}\,\mathrm{erf}\,(\zeta) - \dfrac{n_A}{bt_A}\exp\,(-\zeta^2)\right] + c_2 b}{c_1\sqrt{\dfrac{\pi n_A k_1}{2t_A}}\,\mathrm{erf}\,(\zeta) + c_2} \tag{17}$$

where c_1 and c_2 are constants given by

$$c_1 = \frac{bt_A}{n_A \exp\left(\dfrac{-b^2 k_1 t_A}{2n_A}\right)};\; c_2 = \frac{1 + t_A b\sqrt{\pi}\,\mathrm{erf}\left(b\sqrt{\dfrac{k_1 t_A}{2n_A}}\right)}{\sqrt{\dfrac{2t_A n_A}{k_1}}\exp\left(\dfrac{-b^2 k_1 t_A}{2n_A}\right)},\ \text{and}\ \zeta = \sqrt{\frac{k_1 t_A}{2n_A}}\left(\frac{n_A t}{t_A} - b\right).$$

and erf (ζ) is the error function.

As an example, the number of moles which have reacted at $t = t_A$ under the following conditions are (for 1 litre of solution):

$t = t_A$, *sec*	n_A	b	k_1, *l mole*$^{-1}$. *sec*$^{-1}$	n
1·0	0·01	0·02	50	0·0035
1·0	0·01	0·01	50	0·0019

For the condition $t > t_A$ the reaction will continue as a normal second-order one according to

$$k_1(t - t_A) = \frac{1}{b - n_A} \log \frac{(n_A - n_{t=t_A})(b - n)}{(n_A - n)(b - n_{t=t_A})} \text{ for } n_A \neq b. \tag{18}$$

or

$$k_1(t - t_A) = \frac{1}{n_A - n} - \frac{1}{n_A - n_{t=t_A}} \text{ for } n_A = b \tag{19}$$

In these cases the slope of the curve plotted in the usual way will allow calculation of the correct value of k at $t > t_A$, while the intercept at $t = 0$ will give an erratic value of b_0/n_a.

TIME-LAG OF THE TRANSDUCER

In considering effects connected with the transducer used to follow concentration changes, it must be emphasized that a relatively fast change of input signal may cause output delay and distortion. From the kinetic point of view, this means that t_0, h_0, and the slope of the recorded $f(c)$ *vs.* t curve may be affected. Wyatt[3] has considered the effect of the response time of the galvanometer on a measured first-order kinetic reaction. We consider here a thermistor as transducer.

A glass-covered thermistor generally has a time constant between 0·5 and 10 sec, depending on its insulation shell and the speed of convective motion of the surrounding fluid. The simplified model we tried gives theoretical results in fair agreement with the experimental measurements.

Let us consider that the fluid temperature changes, as in the case of first-order kinetics, according to the law $T = T_0(1 - e^{-k_1 t})$. The temperature change rate of the thermistor will be, according to the Newton heat-exchange law:

$$\frac{\mathrm{d}T_{\text{th}}}{\mathrm{d}t} = k' \, [T_0(1 - e^{-k_1 t}) - T_{\text{th}}] \tag{20}$$

where T_{th} = temperature of the thermistor.

Integrating, we have

$$T_{\text{th}} = T_0 \left[1 + \frac{1}{k' - k_1} (k_1 e^{-k' t} - k' e^{-k_1 t}) \right]. \tag{21}$$

The temperature difference between the fluid and the thermistor at time t will be

$$\Delta T = T_0 \frac{k_1}{k' - k_1} (e^{-k_1 t} - e^{-k' t}). \tag{22}$$

In our experimental conditions the average delay was estimated to be 0·34 sec with magnetic stirring and 0·25 sec with 1500-rpm propeller stirring. The corresponding average values of Newton's constant for the thermistor are 3 sec^{-1} and 4 sec^{-1}.

Figure 1 shows the temperature/time curves for the solution (upper curve) and the thermistor in an exothermic first-order reaction. The corresponding log T *vs.* t plot has a continually changing slope in the initial portion (about 50%) of the curve, and the extrapolated T_0 value is higher than the theoretical one. These effects become larger if the ratio k_1/k' increases.

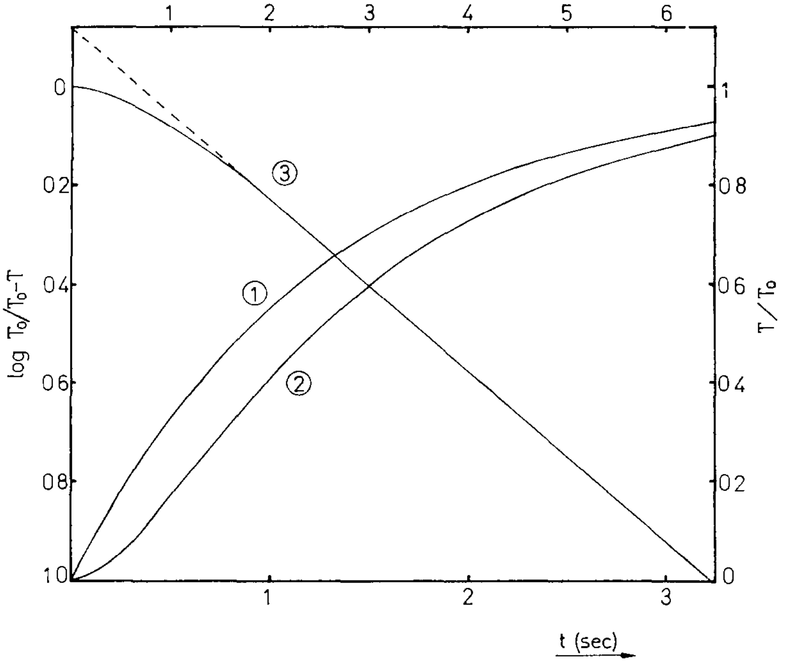

FIG 1 —Effect of the transducer (thermistor) response time on the recorded first-order kinetic reaction curve.

Curve 1—theoretical for $t_A = 0$, $k_1 = 0{\cdot}829$ sec^{-1}, thermistor heat-exchange constant very high, right-hand scale T/T$_0$. Curve 2—the same conditions as curve 1 but a thermistor heat-exchange constant of 3 16 sec^{-1} has been assumed. Curve 3—log $T_0/(T_0 - T)$ *vs.* t; the extrapolated value of the curve at $t = 0$ (dotted line) gives a value of T_0 (proportional to c_0) higher than the theoretical

It was found that the response time of the transducer affects the slope of the curve in the first $3/k'$ sec. After this time the recorded curve will be practically parallel to the theoretical one but with a delay of $1/k'$ sec The delay can be assumed to be approximately given by:

$$\frac{\Delta T}{T_0 k_1 e^{-k_1 t}} = \frac{1 - e^{(k_1 - k')t}}{k^1 - k'} . \tag{23}$$

EXPERIMENTAL

The quasi-adiabatic measurements were made with the apparatus previously described[4] The glass-enveloped thermistor bead was produced by ITT Standard (Switzerland), and had a resistance of 1800 ohm at 25°.

The non-adiabatic measurements were made in a reaction cell 100 mm deep and 50 mm in diameter, drilled in an aluminium cylinder 170 mm high and 180 mm in diameter. To avoid corrosion, the walls of the cell were coated with a thin layer of 18001 Montecatini Edison epoxide resin, which is not affected by the reagents used.

A 1500-rpm helical glass propeller was generally used. The addition time and the mixing time were fixed by the addition of a few ml of reactant to the cell solution, from a 10-ml hypodermic syringe. During its stroke the piston of the syringe activated two microswitches (at the start and at the final injection time) which recorded marks on the upper trace of a 502 A Tektronix oscillograph. The time elapsed between the two marks was the reactant addition time When a controlled-rate addition of the reactant was required, a motor-driven syringe was used.

The mixing time was measured by showing on the lower trace of the oscillograph the output of a resistance bridge containing either a thermistor or a photo-cell as transducer for temperature and colour changes respectively.

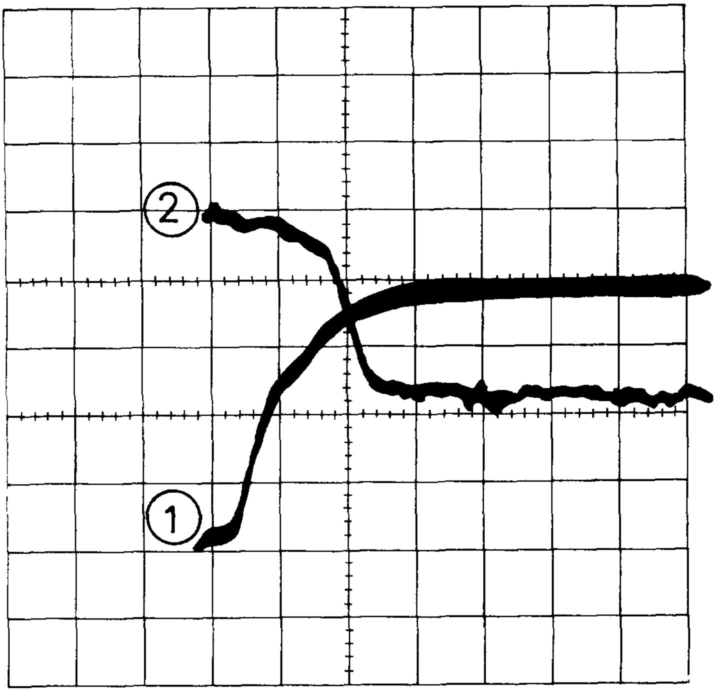

FIG 2.—Mixing-time measurement.

Curve 1—thermistor; curve 2—photo-resistance; sweep 0·5 sec/cm; for other details see text

Figure 2 shows the curves obtained with a photo-resistance (curve 2) and a thermistor (curve 1) for the neutralization of 5 ml of 1*M* sodium hydroxide, 10 drops of 10% phenolphthalein solution and 250 ml of water in the cell, with 5 1 ml of 1*M* hydrochloric acid added from a syringe.

For ideal mixing conditions (instantly achieved homogeneity of the solution during the addition) the change in curve 2 should be very sharp at the time which corresponds to the first excess of acid, curve 1 should rise linearly during the addition and reach the limiting value exactly at the end-point. Experimentally, both curves (curve 1 with a delay not clearly seeable in the figure) reach the limiting value in about 1·5 sec from the beginning of the addition (which itself took about 0 1 sec) * With 40 ml of solution in the reaction cell instead of 250 ml, addition and mixing were completed in about 1 sec.

Finally, the time (1 0–1·5 sec) needed to reach the limiting value was confirmed for the photo-resistance arrangement by addition of 5 ml of alkaline phenolphthalein solution to 250 ml of 0 01*M* sodium hydroxide. In this case the phenolphthalein was already in the red form and the unknown contribution due to its kinetic rearrangement was avoided

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* R Thompson claims[5] that mixing of small volumes by fast injection of one solution into another without stirring takes no more than 30 msec. If the oscilloscope is triggered during the injection according to the statement of the author, it seems from Fig *a* of his paper that mixing requires about 300 msec

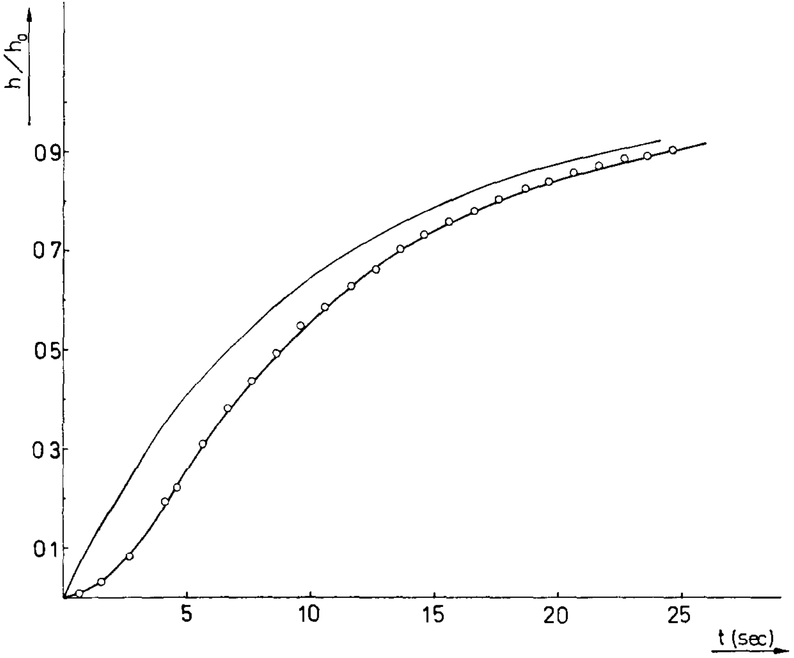

FIG. 3.—Effect of addition time on the recorded curve of methyl acetate hydrolysis at 25°C.

Upper curve (experimental)—t_A = 0·1 sec; lower curve [calculated from equations (4) and (5)] and circles (experimental)—t_A = 4·11 sec. Methyl acetate 0 005*M*, NaOH 0·5*M*.

TABLE I —EFFECT OF ADDITION TIME ON THE EXPERIMENTAL ENTHALPIMETRICALLY MEASURED KINETIC CURVE FOR HYDROLYSIS OF METHYL ACETATE AT 25°C

Quasi-adiabatic									
								$h_{0_{extr}}/h_0$	
[NaOH], *M*	$t_{1/2}$, *sec*	t_A, *sec*	k_1/[NaOH] *l. mole*$^{-1}$. *sec*$^{-1}$	h_0	$h_0 - h_{t_A}/h_0$ measured	calculated	$h_{0_{extr}}$	measured, %	calculated, %
0 50	6·70	4 11	0·207	144 0	0 812	0 812	186 3	25 0	25·0
0 50	6·78	4·26	0·206	153 0	0·836	0 814	193·6	26·5	25 8
0 25	13·35	4·20	0 207	148 5	0 876	0 900	161·4	8 7	11 0
1·00	3·40	0·78	0 202	147·0	0 823	0·930	169 9	11·5	9 0
1·00	3·45	1·77	0·200	122 0	0 828	0 857	147 0	20 5	20 0
0 50	7·00	3·64	0 200	184 5	0 872	0 847	219 0	18 7	19 6
0 50	6·95	3·51	0 200	172 5	0 910	0·850	224·0	22 0	20 0

Non-adiabatic								
[NaOH], *M*	t_{max}, *sec*	t_A, *sec*	k_2 *sec*$^{-1}$	k_1, *sec*$^{-1}$		k_1/[NaOH] *l. mole*$^{-1}$. *sec*$^{-1}$		
1·00	11 44	0 90	0·0294	0·1930*	0·207†	0·193*	0·207†	0 206‡
0 50	18 14	1·68	0·0294	0·0930*	0·101†	0·186*	0 202†	0 206‡
0 25	27·44	3 56	0 0294	0 0444*	0 0506†	0 178*	0 203†	0 206‡

* First-order constant calculated from limit of equation (13) for $t_A = 0$.
† First-order constant calculated from equation (13).
‡ From quasi-adiabatic measurements.

It was surprising to find that the addition and mixing times appeared to be very little affected by changes in the volume and by the type and rotation speed of the propeller.

The time-delay of the thermistor was measured by recording on a Texas two-pen recorder the output of the thermistor bridge and the output of a potentiometer the voltage signal of which was proportional to the volume of reactant added. In other cases the time-delay was measured on the oscillograph.

The error due to the addition time, in a first-order reaction, is shown in Fig 3. The agreement between experimental points (circles) and the calculated curve (unbroken line) is very good. The upper line represents the experimental curve for instantaneous mixing.

Table I gives the apparent and corrected kinetic values compared with the theoretical ones, for various experimental conditions From these results it may be concluded that the mixing time may have a serious effect, depending on the ratio $t_{1/2}/t_A$ and the portion of the $f(c)$ *vs.* t curve considered. The proposed equations can predict the extent of this effect and allow calculation of correct kinetic data from the experimental curves.

Acknowledgement—This work was partly supported by the C N.R Rome.

Zusammenfassung—Der Einfluß der Zugabezeit des Reagens und der Ansprechzeit des Instruments auf registrierte kinetische Kurven wurden betrachtet. Der Einfluß der Mischzeit wurde bei Reaktionen erster und zweiter Ordnung fur den Fall betrachet, daß eine einfache Funktion der Konzentration gemessen wird; bei Reaktionen erster Ordnung auch fur den komplizierteren Fall nichtadiabatischer enthalpimetrischer Messungen. Die vorgeschlagenen Gleichungen erlauben fur jedes Verhältnis der Meschzeit zur Halbwertszeit der Reaktion Berechnung der richtigen Geschwindigkeitskonstanten sowie des Fehlers in der durch Extrapolation aus der experimentellen Kurve berechneten Anfangskonzentration. Ferner zeigen sie, welcher Teil der experimentellen Kurve durch die Mischzeit verfalscht ist und außer Betracht bleiben muß. Die durch die Ansprechzeit eines Thermistors als Konzentrationsfuhler hervorgerufene Verzerrung wurde aus einem vereinfachten Modell berechnet. Die experimentellen kinetischen Messungen durch quasi- und nichtadiabatische Enthalpimetrie stimmen mit den berechneten Werten sehr befriedigend uberein

Résumé—On a considéré l'influence du temps d'addition du réactif et du temps de réponse instrumental sur des courbes cinétiques enregistrées On a considéré l'influence du temps de mélange pour des réactions d'ordres un et deux dans le cas où l'on mesure une simple fonction de la concentration et pour des réactions d'ordre un dans le cas plus complexe de mesures enthalpimétriques non adiabatiques. Pour n'importe quel rapport entre le temps d'addition et le temps de demi-transformation les équations proposées permettent le calcul de la constante de vitesse correcte, de l'erreur dans la concentration initiale calculée extrapolée à partir de la courbe expérimentale et montrent la fraction de la courbe expérimentale qui doit être négligée du fait de l'erreur due à l'influence du temps d'addition. On a calculé la distortion due au temps de réponse d'un thermistor utilisé comme transducteur de concentration à partir d'un modèle simplifié. Les mesures cinétiques expérimentales réalisées par enthalpimétrie quasi- et non adiabatique sont en accord très satisfaisant avec les données théoriques.

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THERMOMETRIC TITRATION OF SOME MONOPROTIC AND DIPROTIC ACIDS IN AQUEOUS AND NON-AQUEOUS MEDIA

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Summary—Some mono- and diprotic acids have been titrated thermometrically with strong alkalis in aqueous and non-aqueous media. Thermograms with sharp arrest points were obtained, from which heats of neutralization were measured. Heats of neutralization in the media used were compared and an effect attributable to hydrogen bonding was found.

THERMOMETRIC titration has been carried out in aqueous and non-aqueous media.[1,2,3] When a reaction proceeds in intermediate stages having different enthalpies, thermometric titration can be used to detect these stages. Diprotic acids would be expected to produce such stages during their reaction with strong alkali, yielding thermograms with two arrest points corresponding to the neutralization of successive carboxylic groups. In the present work some monoprotic and diprotic acids were titrated in aqueous and non-aqueous media, with strong alkali. Thermograms obtained allowed an experimental determination of the enthalpy changes of neutralization.

EXPERIMENTAL

Apparatus

Temperature change was measured by means of two thermistors in a bridge circuit (Fig. 1) A single thermistor bridge of the conventional type[5] was found to suffer from interference caused by the motion of a magnetic stirrer, such interference becoming more marked at high bridge sensitivity. The interference took the form of recorder oscillations corresponding to stirrer speed and was attributed to an induction effect of the rotating magnet on the thermistor leads. Arranging two thermistors in the manner shown prevented this effect and gave a maximum sensitivity of 29 mV/deg, whereas a single thermistor in a similar bridge circuit was found to give 15 mV/deg in the 24–26° range. The bridge was balanced by first adjusting R_1 and R_2 to about 1000 ohms each, then adjusting the ganged pair of resistors. R_2 was then used as a coarse bucking resistor and R_3 as fine control. The unbalanced potential was recorded on a Kent Multilec Mark 3 electronic recorder, range 1 mV. Thermistors used were a matched pair of Standard Telephones and Cables F.23 thermistors with a nominal room temperature resistance of 2000 ohms. The sensitivity of the bridge was dependent on the voltage applied from the potential divider P, which was measured by the voltmeter V. Linearity of unbalanced potential with temperature rise was checked by comparison with a Beckmann thermometer.

The titration vessel was a 100-ml Pyrex beaker insulated in polystyrene, enclosed in a wooden box. The beaker was fitted with a polythene cover held by a threaded polythene flange under the flared beaker mouth. The two thermistors and a small electrical heater were permanently fitted through the polythene cover, which also had a small hole bored in it to allow the burette tip to enter the vessel. The contents of the beaker were stirred by a Teflon covered magnetic stirrer operated by a Gallenkamp S.S. 610 motor. The burette used was a Sargent Model C fitted with a 2·5-ml head, delivering 2·5 ml in 12·5 min. A small electrical heater (2 03 ohm) was made by coiling nichrome wire on two sealed glass tubes. The current was introduced through copper leads and solder connections inside the glass tubes A conventional heater circuit was constructed to provide steady voltage across the heater.

Materials and reagents

Methanol was supplied by B.D.H. (water content <0·01%, recommended for Karl Fischer and non-aqueous titration). Analytical grade benzene was used. Benzoic acid (Hopkins and Williams) was of British Chemical Standards No. 190h quality, intended for use in calorimetry, 99·99% pure. Phthalic, salicylic, isophthalic, malonic, succinic, glutaric, adipic, maleic, fumaric, tartaric, and boric acids were reagent grade purified by recrystallization from water until their melting points were within 1° of literature values.[4] Oxalic acid was anhydrous analytical grade. Titrant sodium hydroxide solution was made by adding washed analytical grade sodium hydroxide pellets to water, the product being about $2M$. Titrant sodium methoxide solution was made by adding clean sodium to 300 ml of methanol until reaction was very slow, then adding 200 ml of methanol, the final product being about $1{\cdot}5M$. Titrant tetra-n-butylammonium hydroxide solution was made by shaking 120 g of dry tetra-n-butylammonium iodide with 70 g of dry silver oxide in 500 ml of methanol for one week, allowing to settle, and filtering off the clear solution. The final solution was about $0{\cdot}5M$ and found to be stable although pale yellow. All titrants were stored in insulated amber glass bottles with protection against carbon dioxide and water vapour.

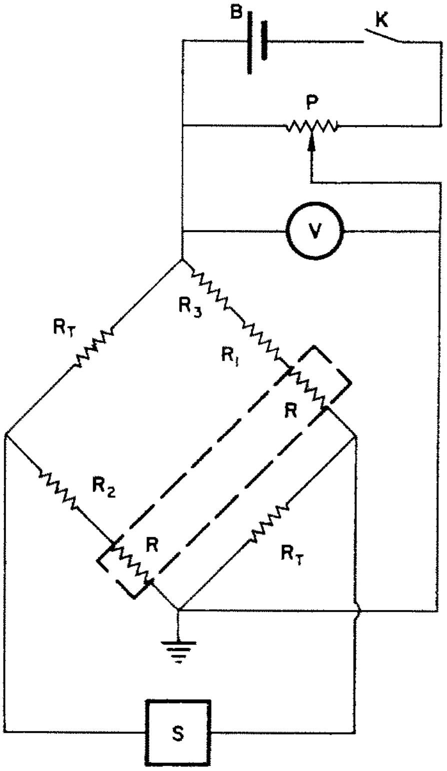

Fig 1.—Apparatus.
B—1·5 V dry-cell; *K*—key switch; *V*—voltmeter (3 V), *R*—ganged pair 2000 Ω. variable resistors; R_1, R_2—2000 Ω variable resistors; R_3—100 Ω variable resistor, R_T—S.T.C. F.23. thermistors; *P*—potential dividers, 2000 Ω; *S*—Kent Multilec recording potentiometer.

Method

The stirrer and a weighed amount of acid were placed in the 100 ml beaker and 50 ml of solvent added from a pipette. The cover with its attached thermistors and heater was fitted, then beaker and contents were placed in the insulating box and allowed to come to thermal equilibrium while being stirred. When the thermistor bridge-recorder gave a steady trace the burette tip was introduced. In aqueous titration a small plug of silicone grease in the burette tip prevented mixing of titrant and titrand before the burette motor was started to perform the titration. In non-aqueous titration an air space was left between titrant and burette tip to ensure no pre-titration mixing occurred, as silicone grease was dissolved by the titrants employed. Recorder speed was arranged to produce a thermogram about 20 cm long for each titration. A suitable bridge sensitivity was chosen by trial. Initial titration with benzoic acid as standard was used to calibrate the delivery of the burette in mmole of titrant per cm of chart run. This value was then used to calculate the amount of titrant added in subsequent titrations, from measurement of chart length. Titration time was 3–6 min.

The thermograms produced deviated only slightly from linearity so that the enthalpy change of neutralization was measured by an extrapolation method[5] rather than the initial slope method. In experiments to determine enthalpy change the recorder was run at minimum speed (16 in./hr), the amount of acid used was reduced, and bridge sensitivity adjusted in order that titration time would be small and a steep thermogram produced, minimizing errors of extrapolation. The apparatus was calibrated for enthalpy determination by heating the 50 ml of titrant solution stirred in its insulating vessel at a known wattage for a known time as the recorder trace was produced. The height of the resultant thermogram was corrected by extrapolation, and a calibration factor calculated in calories per cm rise on the thermogram. Calibration was performed before and after each titration and a mean value taken for calculation. Heater current was adjusted so that the slope of a calibration thermogram was almost the same as that of its titration thermogram. At least three titrations were performed for each ΔH° value reported. The accuracy of the enthalpy determination method was checked by titrating potassium chloride into silver nitrate solution with the apparatus and comparing the results for ΔH_{AgCl} with literature values obtained in a like manner[6,7] (determined value −15·8 kcal/mole; literature value[7] −15·8 kcal/mole).

All titrations were carried out at room temperature, 20 ± 2°.

RESULTS

Results are summarized in Tables I, II and III.

Titration in all solutions produced almost linear thermograms with easily detected arrest points. Benzoic acid was a satisfactory standard in the solvent employed for calibrating the burette delivery, yielding but one equivalence point, no precipitates, and sharp arrest points. Aqueous titration of phthalic, oxalic, malonic, and succinic acids produced thermograms showing two arrests corresponding to the successive

TABLE I.—TITRATION OF ACIDS IN AQUEOUS SOLUTION WITH SODIUM HYDROXIDE

Acid	pK_a*	Ratio found/added	Ratio 2nd arrest/1st arrest	Replicates	Relative std. devn., %	ΔH°† *kcal/mole*
Benzoic	4·19	1·000		6	0·65	−13·9
Salicylic	2·97	1·006		5	1·2	−13·4
Phthalic	2·89	0·991	1·98	7	0·9	−14·4
	5·51					−13·7
Oxalic	1·23	0·976	1·88	5	2·0	−13·5
	4·19					−14·6
Malonic	2·83	1·008	2·00	6	0·50	−14·6
	5·69					−15·1
Succinic	4·16	1·001	1·97	5	2·2	−13·2
	5·61					−14·0
Glutaric	4·34	1·018		2	0·65	
	5·41					−28·6
Adipic	4·43	0·982		3	2·1	
	4·41					−28·8
Maleic	1·83	1·010		5	1·4	
	6·07					−28·4
Fumaric	3·03	0·995		2	0·7	
	4·44					−28·5
Tartaric	2·98	1·022		3	1·6	
	4·34					−27·3
Boric	9·14	1·014		3	1·1	−10·2

Bridge voltage 0·4 V; 0·3 mmole of acid in 50 ml of solution; 0·03205 mmole of NaOH per cm of chart; chart speed 4 in./min for titration, 16 in./hr for ΔH° measurements.

* Literature values; reference 4.

† ±0·2 kcal/mole.

TABLE II.—TITRATION OF ACIDS IN METHANOL WITH SODIUM METHOXIDE

Acid	Ratio found/added	Ratio 2nd arrest/1st arrest	Replicates	Relative std. devn., %	$\Delta H°$‡ *kcal/mole*
Benzoic	1·000		8	0·83	−7·0
Salicylic	0·992		3	0·42	−7·1
Phthalic	0·998	1·99	5	0·83	−6·5 −7·2
Isophthalic	1·013	2·08	4	0·90	−7·2 −6·0
Oxalic	0·997*	2·00	5	0·60	−8·4 −6·2
Malonic	0·999	2·00	5	1·5	−6·5 −7·2
Succinic	0·996	2·06	5	0·62	−6·3 −7·3
Glutaric	1·001		5	0·72	−13·4
Adipic	1·003	2·06	3	0·90	−7·4 −6·3
Maleic	0·991	2·00	5	0·58	−8·8 −4·6
Fumaric	0·989†		3	1·45	
Tartaric	0·987	1·95	3	0·42	−6·6 −6·1
Boric	1·004		4	0·23	−13·9

Bridge voltage 0·1 V (0·4); 1·0 mmole (0·3) of acid in 50 ml of solution; 0·1001 mmole of CH_3ONa per cm of chart; chart speed 64 in /hr (16); figures in brackets refer to $\Delta H°$ measurements, others to titrations.

* White precipitate formed.

† Precipitate formation distorts thermogram

‡ ±0·2 kcal/mole

TABLE III.—TITRATION OF ACIDS IN METHANOL–BENZENE WITH TETRA-n-BUTYLAMMONIUM HYDROXIDE

Acid	Ratio found/added	Ratio 2nd arrest/1st arrest	Replicates	Relative std. devn., %	$\Delta H°$* *kcal/mole*
Benzoic	1·000		8	0·55	−5·9
Salicylic	1·012		4	0·67	−5·7
Phthalic	1·013	1·99	5	0·50	−4·4 −5·7
Isophthalic	0·967	1·97	3	0·77	−6·4 −5·1
Oxalic	0·984	2·03	3	0·95	−8·6 −9·9
Malonic	1·000	1·99	4	1·08	−5·6 −8·4
Succinic	0·987	2·04	3	0·57	−3·8 −8·6
Glutaric	0·994	2·00	3	0·86	−5·8 −6·9
Adipic	1·004		3	0·09	−11·7
Maleic	0·996	1·95	3	1·2	−7·6 −5·2
Fumaric	0·984	2·03	3	1·2	−7·0 −5·6
Tartaric	0·965	2·20	3	2·1	−4·2 −6·2
Boric	0·995		3	0·65	−13·6

Bridge voltage 0·15 V (0·4), 0·5 mmole (0·3 of acid in 50 ml of solution; 0·05215 mmole of $(C_4H_9)_4NOH$ per cm of chart, chart speed 64 in /hr (16); figures in brackets refer to $\Delta H°$ measurements, others to titrations.

* ±0·2 kcal/mole.

neutralization of the acid groups. Thermograms became steeper after the first arrest in the case of aqueous oxalic, malonic, and succinic acids, but less steep in the case of aqueous phthalic acid. The other diprotic acids examined showed no intermediate arrests in aqueous titrations (Fig. 2). When intermediate steps were detected the enthalpy change for each neutralization was found, otherwise the values in the tables are those of both the acid groups together. Aqueous boric acid was monoprotic, its arrest point being rounded but allowing accurate location of equivalence. The $\Delta H°$ value found (−10·2 kcal/mole) is in exact agreement with literature values.[8]

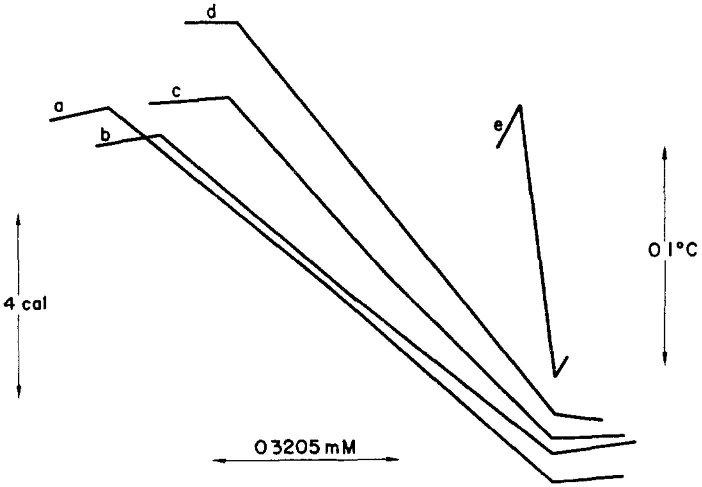

Fig. 2.—Thermograms for titration of sodium hydroxide solution into 50 ml of aqueous solution of various acids.
a—0·3636 mmole of phthalic acid; *b*—0·3166 mmole of succinic acid; *c*—0·2727 mmole of oxalic acid; *d*—0·2679 mmole of maleic acid; *e*—0·780 mmole of boric acid (for ΔH determination)

The successive $\Delta H°$ values (−13·5 and −14·6 kcal/mole) for oxalic acid were found to agree closely with literature values[7] (−13·4 and −14·5 kcal/mole). The $\Delta H°$ values for neutralization of a single carboxylic acid group were all between −13 and −15 kcal/mole.

Titration in methanol with sodium methoxide in methanol as titrant allowed detection of successive neutralizations in the case of all the diprotic acids examined except glutaric acid. Phthalic, malonic, and succinic acid gave thermograms rising more steeply after the first arrest. White precipitates were produced during titrations with oxalic acid and fumaric acid, which in the latter instance distorted the linearity of the thermogram, preventing detection of successive neutralization but allowing a sharp final arrest point.

$\Delta H°$ values were more variable than those found in aqueous titration, maleic acid having the biggest difference in successive values. Boric acid was monoprotic, had a slightly rounded arrest point which allowed accurate end-point location, and a $\Delta H°$ value considerably greater than the other acids.

For titration with tetra-n-butylammonium hydroxide dissolved in methanol the acids were dissolved in 1:4 methanol–benzene mixture. This proportion of methanol in the solvent was found to eliminate effects of heat of dilution and mixing which were observed in preliminary experiments when benzene alone was used as solvent.

Such effects would not influence titrations carried out primarily for estimation but would impair those in which ΔH° was determined. Experiment showed that with this solvent mixture, the introduction of the 0·5M titrant had no measurable effect on the linearity of the thermograms at the bridge sensitivity used. Thermometric titration was found to be a successful means of finding equivalence points in this medium. Thermograms were almost linear, with easily located arrest points occurring at equivalence. Phthalic, oxalic, malonic, succinic, glutaric, and tartaric acids produced thermograms rising more steeply after the first arrest. Phthalic and maleic acids had rounded final arrest points but these allowed equivalence to be determined. Titration with salicylic acid gave an unusual inflection immediately before the final arrest point. This inflection effect was also observed at the first arrest for phthalic, maleic, and malonic acids but not in any other cases (Fig. 3). ΔH° values showed greater variation than in the other solvents, succinic acid having the biggest difference between successive values. The ΔH° value for boric acid was much greater than those of the other acids, and was the same as that found in methanol. Boric acid gave a slightly rounded arrest point and was monoprotic.

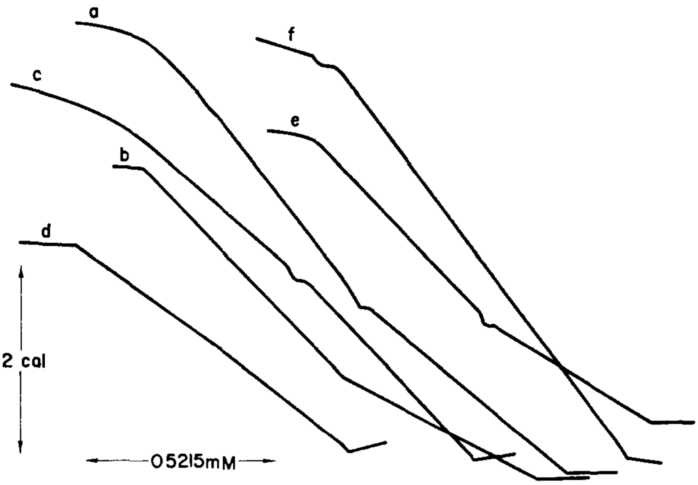

FIG. 3.—Thermograms for titration of tetra-n-butylammonium hydroxide in methanol into 50 ml of 1:4 methanol—benzene solution of various acids.
a—0·5962 mmole of phthalic acid; *b*—0·5744 mmole of succinic acid; *c*—0·5559 mmole of maleic acid; *d*—0·4048 mmole of fumaric acid; *e*—0·5016 mmole of malonic acid; *f*—0·9088 mmole of salicylic acid.

DISCUSSION

Tyrrell has devised a method of calculating the feasibility of thermometric titration giving a sharp arrest point when used in a neutralization reaction.[9] Values of Tyrrell's function ζ calculated from Table I show that, apart from boric acid, all the titrations in aqueous solution should give thermograms with sharp arrest points, a prediction borne out by the results. Under the conditions used ζ for boric acid was about 10^{-3}, implying a rounded but accurate end-point, which was observed in practice. Titration in aqueous solution showed that ΔH° values for neutralization of a single carboxylic group do not differ appreciably from the value for "strong acid-strong base" neutralization (−13·5 kcal/mole) and are not greatly affected by the dissociation constant (K_a) for the carboxylic group. This shows that the enthalpy change of ionization ($\Delta H_i°$) is low for the carboxylic groups in the acids studied. $\Delta H_i°$ is related to the dissociation constant of the acid by the relationship $\Delta H_i° = T\Delta S_i° - RT\ln K_a$. In a study of thermometric titration of weak monoprotic acids in aqueous solution with aqueous sodium hydroxide, Jordan and Dumbaugh[10] concluded that if K_a were small the $\Delta H_i°$ value would be compensated by $\Delta S_i°$ being correspondingly larger, and on this basis they calculated $\Delta S_i°$ values. The present work shows a similar effect in diprotic acids so that even if successive dissociation constants for such acids are very different, *e.g.*, for maleic acid, the values of $\Delta H°$ for successive neutralizations are almost same. In some cases the second $\Delta H°$ value exceeds the first.

In non-aqueous solvents with a lower dielectric constant and autoprotolysis constant than water, hydrogen bonding and electrostatic effects would be stronger, resulting in different entropy changes from those found in aqueous media. Titration in non-aqueous media would be expected to show $\Delta H°$ values different from and showing more variation than those in the corresponding aqueous titration. Results obtained showed such changes.

The inflections found in the tetra-n-butylammonium hydroxide titration curves occurred with those acids in which stabilization of the anion formed by removal of the first proton can be brought about by intramolecular hydrogen bonding (*e.g.*, salicylic acid, Fig. 4).

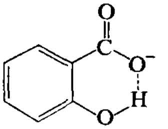

FIG. 4

An anomaly in the shape of potentiometric and conductimetric curves for weak acids titrated in non-aqueous solvents with tetra-n-butylammonium hydroxide has been observed and accredited to the formation of hydrogen-bonded dimers between the ionic and non-ionic forms of the acids,[11,12] such a compound having been isolated.[13] An explanation of the present inflection with salicylic acid could be the energy change due to the formation of a metastable hydrogen-bonded associated species between the non-ionized dimer present in the solvent of low dielectric constant (Fig. 5) and the

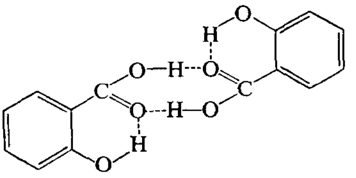

FIG. 5

intramolecularly hydrogen-bonded salicylate ion. The position of the inflection shows that the conditions conducive to this arrangement are a preponderance of the intramolecularly bonded ion. The second neutralization after such inflections in the case of diprotic acids will be that of the intramolecularly hydrogen-bonded ion, the rounded arrest point showing that this species is an extremely weak acid, but the entropy change keeps ΔH° of neutralization the same as that of the other acids studied. A similar explanation can apply to the inflections of the thermograms of phthalic, malonic, and maleic acids.

The rounded arrest point for boric acid in non-aqueous solvents shows that in them it is a very weak acid. Nevertheless the ΔH° value is very high, showing that the entropy change is considerable in such solvents.

Zusammenfassung—Einige ein- und zweibasige Sauren wurden thermometrisch mit starken Alkalien in waßrigen und nichtwaßrigen Medien titriert. Es wurden Thermogramme mit scharfen Haltepunkten erhalten, aus denen die Neutralisationswarmen ermittelt wurden. Die Neutralisationswarmen in den verwendeten Medien wurden verglichen und ein auf Wasserstoffbindung zuruckzufugrender Effekt gefunden.

Résumé—On a titré thermométriquement quelques acides mono et diprotiques avec des alcalis forts en milieux aqueux et non aqueux. On a obtenu des thermogrammes avec des points d'arrêt nets, à partir desquels on a mesuré les chaleurs de neutralisation. On a comparé les chaleurs de neutralisation dans les milieux utilisés et l'on a trouvé une influence attribuable à la liaison hydrogène.

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ANALYTICAL APPLICATIONS OF TERNARY COMPLEXES—VI*

SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF PALLADIUM

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Summary—Extremely sensitive and specific colour reactions in both aqueous and organic solutions are described for the spectrophotometric determination of palladium(II) ions. The methods are based upon ternary complex formation with 1,10-phenanthroline or pyridine, and Rose Bengal Extra. The molar absorptivities are 5×10^4 (aqueous) and $1{\cdot}25 \times 10^5$ (organic) in the presence of a 1000-fold molar excess of EDTA as mass masking agent. Under these conditions there is negligible interference with the pyridine–Rose Bengal Extra system from the 22 cations (including silver, gold and platinum) and seven anions investigated. Both colour reactions take place within 15 min and the complexes are stable for long periods.

THE importance attached to the determination of the noble metals is reflected in the very large number of methods described in the literature, especially for palladium. Many review articles assess the various methods and enable the analyst to select the most appropriate, *e.g.*, that by Beamish[1] in 1965. He concluded that the majority of methods proposed dealt with improvements in selectivity towards palladium. Molar absorptivities below 5×10^4 are commonplace, and values as low as 1600, *e.g.*, with dimethylglyoxime,[2] are to be found. Those methods with attractive sensitivities usually suffer from quite serious interferences. For example, the *p*-dimethylaminobenzylidenerhodanine[3,4] and 2-nitroso-1-naphthol-4-sulphonic acid[5] procedures are subject to interference from cobalt, nickel and the other noble metals. In addition, cyanide and iodide interfere with the former, and iron and chromium with the latter. The most sensitive method described to date utilizes *p*-nitrosodiphenylamine.[6,7] Ryan[6] obtained a molar absorptivity of $6{\cdot}5 \times 10^4$, using chloroform as an extractant. Oxidizing agents, gold and small amounts of platinum and iodide interfere.[8] *p*-nitrosodimethylaniline[9] yields a similar sensitivity and the colour development in this instance is instantaneous. However, the former reagent can be used over a wider concentration range and is, therefore, preferred in practice.

More recently, in 1967, Sen Gupta[10] described the use of arsenazo III for the spectrophotometric determination of palladium and reported a molar absorptivity of $1{\cdot}26 \times 10^5$. The procedure involved evaporation of the complex to dryness on a steam-bath and dissolution of the residue. Colour development required *ca.* 1 hr. Other workers,[11] however, reported that the molar absorptivities of the palladium(II)–arsenazo III complexes were only *ca.* $4{\cdot}2 \times 10^4$ and $1{\cdot}6 \times 10^4$ at 630 and 620 nm respectively. They also found that the method was subject to interferences from copper, cobalt, nickel, thorium, uranium and the rare earths. These same workers[12]

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* Part V, *Talanta*, 1968, **15**, 107.
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therefore proposed and synthesized a new and more selective reagent for palladium, known trivially as "palladiazo" [2,7-bis-(4-azophenylarsono)-1,8-dihydroxynaphthalene-3,6-disulphonic acid]. The molar absorptivities were $3{\cdot}3 \times 10^4$ and $1{\cdot}7 \times 10^4$ at 540 and 635 nm respectively. Bismuth, cerium, lead and the rare earth elements still interfered.

In our study of ternary complex formation, we have found that the palladium(II) ion may be determined with advantage by using ternary complex systems similar to those described previously in this series.[13–17] The only other instance of ternary complex formation involving palladium and known to us is that described by Forsythe, Magee and Wilson.[18,19] This method utilizes the $[Pd(pyridine)_2]^{2+}[(SCN)_2]^{2-}$ complex and is one of the most selective methods for palladium because it allows its determination in the presence of the other noble metals. However, the sensitivity of this reaction is rather low.

EXPERIMENTAL

Colour reaction

The addition of many bivalent ions to a near neutral aqueous solution of 1,10-phenanthroline and Rose Bengal Extra (RBE) produces a change in the wavelength of maximum absorption from 535 to 575 nm.[14,15] The small wavelength shift is compensated for by the sharpness of the absorption bands. Palladium gives such a colour reaction with a molar absorptivity of *ca.* 5×10^4. The use of pyridine instead of 1,10-phenanthroline does not produce any colour change with palladium in aqueous solution, but it does give rise to a stable chloroform-extractable species with a maximum wavelength of absorption at 570 nm. In near neutral solution the excess of dyestuff is not extracted and the molar absorptivity is $1{\cdot}25 \times 10^5$. Similar reactions are given with other anionic dyestuffs, *e.g*, Bromophenol Blue and Bromopyrogallol Red, but the sensitivity is not as high. Erythrosin may be used in place of RBE with only a slight loss in sensitivity

The mechanism of these colour reactions, which probably involves the production of micelles, will be the subject of a further communication.[20] However, both reactions involving RBE were examined in more detail because of the need for very sensitive colour reactions, particularly in aqueous solution.

Effect of pH

The reaction in aqueous solution with 1,10-phenanthroline gave maximum colour development over the pH range 5–6·5. The absorbance was measured at 575 nm against a similar solution, which contained no palladium(II) ions.

Similar solutions containing pyridine instead of 1,10-phenanthroline were extracted with 25 ml of chloroform. In this instance the pH of the aqueous phase for maximum absorbance at 570 nm was more sharply defined as pH 7 5–8.

Time for colour development

The reaction in aqueous solution took place instantaneously and the product was stable under normal laboratory conditions for at least 48 hr. Maximum colour development of the extracted palladium(II)–pyridine–RBE required about 15 min after extraction into chloroform. The complex was stable for at least 5 hr. In both instances the order of reagent addition was unimportant.

Examination of interfaces

Since RBE does not contain an arrangement of groups suitable for the formation of metal complexes, interferences may be expected only from those ions which form complexes with 1,10-phenanthroline. Experience has shown that most of these ions can be masked with EDTA,[18] and provided that the resulting complexes do not absorb appreciably at 575 nm then there should be negligible interference in the colour reaction with Rose Bengal Extra. It was established that a 10000-fold molar excess of EDTA over palladium caused no interference and was capable of masking effectively a 10-fold molar excess of Au(III) and Pt(IV).

A more detailed examination was carried out with the palladium(II)–pyridine–RBE complex by extracting the ternary complex and measuring the absorbance at 570 nm Table I shows the results obtained for 22 cations and 7 anions. Of those ions capable of being masked with EDTA, only gold (in 100-fold molar excess) interfered; however, a 10-fold excess of gold caused only a 2% change in absorbance and was considered not to interfere. The other ions tested all gave less than 5% change in the absorbance (*i.e.*, less than twice the relative standard deviation). Silver was masked by the excess of chloride ion present in the palladium(II) chloride solution and not by the EDTA.

TABLE I —INTERFERENCE STUDY

Ion added	Molar excess over palladium	Absorbance (*vs.* blank) at 570 nm	Deviation
Pd(II) (standard)		0·505	
Ag	100	0·535	+0·030
Al	100	0·500	−0·005
Au(III)	100	0·540	+0·035
Ba	100	0·515	+0·010
Ca	100	0·500	−0·005
Cd	100	0·510	+0·005
Co(II)	100	0·520	+0·015
Cu(II)	100	0·495	−0·010
Fe(III)	100	0·495	−0·010
Hg(II)	100	0·530	+0·025
K	1000	0·502	−0·003
La	100	0·500	−0·005
Li	100	0·510	+0·005
Mg	100	0·502	−0·003
Mn(II)	100	0·510	+0·005
Na	1000	0·500	−0·005
Nb(V)	100	0·485	−0·020
Ni	100	0·520	+0·015
Pb	100	0·517	+0·012
Pt(IV)	100	0·492	−0·013
V(V)	100	0·495	−0·010
Zn	100	0·490	−0·015
Cl^-	1000	0·502	−0·003
ClO_4^-	100	0·510	+0·005
CO_3^{2-}	100	0·500	−0·005
F^-	1000	0·500	−0·005
HPO_4^{2-}	10000	0·505	0·000
NO_3^-	100	0·530	+0·025
SO_4^{2-}	100	0·490	−0·010

Beer-Lambert law

Under the established optimized conditions, linear calibration curves were obtained from 1–20 ppm for the aqueous palladium(II)-1,10-phenanthroline–RBE complex and from 0·2–10 ppm for the extracted pyridine complex. The respective molar absorptivities were 5×10^4 at 575 nm and at $1·25 \times 10^5$ 570 nm. The relative standard deviations for 10·67 μg of palladium were 1·4% and 2·4% for the (1,10-phenanthroline and pyridine systems respectively.

Nature of complex

By analogy with similar studies[13–17] the complex in aqueous solution is most probably $(Pd\text{-}phen_2)^{2+}$ RBE^{2-} (*i.e.*, 1:2:1). The purity of Rose Bengal Extra is not sufficiently high,[14] however, to allow an accurate determination of the reagent ratios by the usual methods. A thorough study of this type of reaction and the colour changes involved will be given later.[20]

The ternary complex with pyridine is a relatively new system, however, and was considered in more detail. The results may be summarized as follows.

(*a*) Mole-ratio studies of the Pd(II): pyridine ratio in presence of excess of RBE under optimum conditions gave steadily increasing absorbance readings up to a ratio of 1:10000. This suggests weak complex formation. There were no observed breaks in the curve.

(*b*) A Job plot for a constant total molar concentration of palladium(II) and Erythrosin (*i.e.*, tetraiodofluorescein of known purity) in presence of excess of pyridine indicated a ratio of 1:1 as predicted by theory. This closely related dyestuff was used in place of RBE because a pure sample of it was available. It gives a colour reaction with palladium and pyridine similar to that with RBE, but a slightly lower sensitivity. A disadvantage is that it gives a much higher blank value than RBE and is less sensitive in aqueous solution.

We conclude that the extracted complex is $[(Pd\text{-}py_2)^{2+} RBE^{2-}]$ or $[(Pd\text{-}py_4)^{2+} RBE^{2-}]$, *i.e.*, 1 2 1 or 1 4 1 In view of the findings of other workers, investigating the palladium-pyridine-thiocyanate complex,[19,20] the more likely ratio is 1 2 1.

Reagents

Palladium(II) *chloride*, $10^{-2}M$. Dissolve 0 8805 g of palladium(II) chloride in 10 ml of concentrated hydrochloric acid and dilute to 500 ml with distilled water. Standardize the solution by adding excess of EDTA and back-titrating with standard zinc solution, using Xylenol Orange as indicator. Dilute the solution as required

1,10-Phenanthroline, $10^{-2}M$. Dissolve 0 991 g of 1,10-phenanthroline hydrate in 500 ml of distilled water.

Pyridine, 10% w/v aqueous solution.

Rose Bengal Extra, $2 \times 10^{-4}M$. Dissolve 0 1018 g of RBE in 500 ml of distilled water.

EDTA, 0 1*M*

Acetate buffer solutions, pH 6 and pH 8

Procedures

Aqueous solution (1–20 *ppm*). Place the sample [equivalent to 1–20 ml of $10^{-5}M$ palladium(II)] in a 50-ml volumetric flask and 1 ml of $10^{-2}M$ 1,10-phenanthroline, 1 ml of 0 1*M* EDTA, 2 ml of pH 6 acetate buffer and 5 ml of $2 \times 10^{-4}M$ Rose Bengal Extra. Dilute to the mark with distilled water and measure the absorbance at 575 nm in a 1-cm cuvette against a reagent blank. Prepare a calibration curve covering the range 1–20 ml of $10^{-5}M$ palladium.

Extraction method (0 2–10 *ppm*). Transfer the sample corresponding to 2–5 ml of $10^{-6}M$ palladium (or 1–10 ml of $10^{-5}M$ for higher ranges), 1 ml of 10% pyridine solution, 2 ml of pH 8 acetate buffer, 1 ml of 0 1 *M* EDTA, 5 ml of $2 \times 10^{-4}M$ Rose Bengal Extra and sufficient distilled water to give a volume of about 20 ml, into a 100-ml separating-funnel. Add 15 ml of chloroform, shake for *ca* 1 min and, after a further 15 min, transfer part of the organic phase into a clean dry 1-cm cuvette and measure the absorbance at 570 nm against a reagent blank.

CONCLUSIONS

The methods proposed are simple, rapid, and sensitive. Both compare very favourably with most of the published methods for the determination of palladium, and they can certainly be classified amongst the most sensitive published methods.

Although the nitrosodimethylaniline and the *p*-nitrosodiphenylamine methods are the most sensitive methods to date, both suffer interferences from cobalt(II), gold(III), iron(III), iridium(IV), nickel(II), platinum(IV) and rhodium(III), neutral salts, and oxidizing and reducing agents.[9]

In the proposed 1,10-phenanthroline–RBE method the colour is formed instantaneously and remains stable for more than two days under normal laboratory conditions. The procedure can tolerate small amounts of gold(III) and platinum, *i.e.*, up to 10-fold molar excess over palladium(II), by use of EDTA as a masking agent.

The pyridine-RBE method is extremely sensitive (molar absorptivity $1{\cdot}25 \times 10^5$) and selective. Palladium(II) ions can be determined in the presence of 100-fold molar excess of 22 other cations if EDTA is used. Seven common anions, carbonate, chloride, fluoride, phosphate, nitrate, perchlorate and sulphate, were found not to interfere.

Zusammenfassung—Extrem empfindliche und spezifische Farbreaktionen in wäßrigen und organischen Losungen werden zur spektrophotometrischen Bestimmung von Palladium(II)-Ionen beschrieben. Die Methoden bruhen auf der Bildung ternarer Komplex mit 1,10-Phenanthrolin oder Pyridin und Rose Bengale Extra. Die molaren Extinktionskoeffizienten sind 5 10^4 (in waßriger Losung) und $1{,}25{\cdot}10^5$ (in organischer Losung) in Gegenwart eines 1000-fachen molaren Überschusses von EDTA als Maskierungsmittel Unter diesen Bedingungen sind

Storungen des Systems Pyridin Rose Bengale Extra durch die untersuchten 22 Kationen (darunter Silber, Gold und Platin) und 7 Anionen vernachlassigbar. Beide Farbreaktionen finden in 15 Minuten statt; die Komplexe sind uber langere Zeitraume haltbar.

Résumé—On décrit des réactions colorées extrêmement sensibles et spécifiques tant en solutions aqueuses qu'organiques pour le dosage spectrophotométrique des ions palladium(II). Les méthodes sont basées sur la formation de complexes ternaires avec la 1,10-phénanthroline ou la pyridine, et le Rose Bengale Extra. Les coefficients d'absorption moléculaire sont 5×10^4 (aqueux) ou $1{,}25 \times 10^5$ (organique) en la présence d'un excès 1000 fois molaire d'EDTA comme agent de dissimulation de masse. Dans ces conditions, avec le système pyridine-Rose Bengale Extra, l'interférence des 22 cations (comprenant l'argent, l'or et le platine) et des 7 anions étudiés est négligeable. Les deux réactions colorées se produisent en 15 mn et les complexes sont stables pendant de longues périodes.

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ANALYTICAL APPLICATIONS OF TERNARY COMPLEXES—VII*

ELUCIDATION OF MODE OF FORMATION OF SENSITIZED METAL-CHELATE SYSTEMS AND DETERMINATION OF MOLYBDENUM AND ANTIMONY

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Summary—The ternary complexes which are formed when surface-active agents are added to various metal–dyestuff chelate systems are shown to be dependent on the formation of micelles. Spectrophotometric measurements indicate that true ternary complexes are formed with well defined structures and that the changes in absorption spectra produced are not due to simple adsorption of the binary metal-dye complex onto micellar aggregates. Some suggestions are made to account for the nature of the observed changes. The analytical potentialities of this type of system are illustrated by the formation of such complexes between molybdenum or antimony, Catechol Violet and cetyltrimethylammonium bromide, yielding molar absorptivities of $4 \cdot 6 \times 10^4$ and $3 \cdot 0 \times 10^4$ respectively.

FOR a number of years we have been concerned with increasing the sensitivity of molecular absorption spectrophotometry (MAS) as a means of achieving trace metal determination. The "natural" sensitivity of MAS is limited both in practice and theory *e.g.*, the minimum measurable absorbance is about 0·002, and the maximum molar absorptivity is about 10^5, and MAS is less sensitive than molecular fluorescence spectrophotometry (MFS). It has been our aim to develop a highly sensitive general reaction mechanism for determination of many elements by MAS. Our approach towards achieving selectivity has been largely through the use of masking agents and solvent extraction.

We have concentrated on the use of ternary systems in which one of the components is a strongly absorbing dyestuff molecule. The sensitivity of the colour reaction is then largely due to the dyestuff molecule, which may have a molar absorptivity approaching 10^5. In addition, because of the nature of the dyestuff molecule, some of the methods have been well suited for MFS.

The first type of complex developed by us was the ion-association system of a metal–1,10-phenanthrolinium cation coupled to the anion of a dyestuff such as Bromopyrogallol Red (BPR).[1,2] Later we preferred dyestuff molecules without complexing centres, such as tetraiodo(R)tetrachloro(P)fluorescein (Rose Bengal Extra).[3,4] In both instances a bathochromic shift occurs in the absorption maximum of the reagent on complex formation. With BPR the change is from 560 to 635 nm and there is negligible interference from the reagent because the absorption bands are

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narrow. With Rose Bengal Extra (RBE), however, the change is only about 30 nm (540 to 570 nm) and so it is better, for analytical purposes, to extract the complex into organic solvents and leave the unreacted organic dyestuff in the aqueous phase. This extraction is favoured by the carboxylic acid group in RBE. On the other hand, the BPR ternary complexes, which contain a sulphonic acid grouping, can only be extracted into nitrobenzene.

The physical nature of both ternary complexes is similar; they precipitate from aqueous solution if left overnight or if concentrated solutions are used, and have definite molecular ratios in both the aqueous and organic phase. The first factor, together with the fact that the colour changes in aqueous solution were those obtained when the dyestuffs were used as adsorption indicators, suggested that the reaction mechanism might be *via* adsorption of the dyestuff molecule onto a precipitated species involving the metal–phenanthroline complex. However, the definite molecular ratios and the ease of extraction suggest a somewhat different mode of reaction. The colour changes alone suggest that something other than simple ion-association is involved.

More recently we have used binary metal ion complexes of organic dyestuffs such as Catechol Violet, "sensitized" by the addition of the long-chain cationic surfactant cetyltrimethylammonium bromide (CTAB).[5] This mode of reaction is considered by us to be more generally applicable and one of the most sensitive methods available for the absorptiometric determination of many metal ions. A certain similarity in behaviour was noted between these systems and the ternary complexes previously described. In view of their analytical potential we have, therefore, made an attempt to define the reaction mechanisms and their associated colour changes.

Somewhat similar systems have been described by other workers. Malát[6] has utilized the "partial" sensitization of the tin–Catechol Violet complex with gelatin as a method for the determination of tin. He gave no indication of the reaction mechanism, and we have found that the use of cetyltrimethylammonium bromide is superior.[5] Malát has since extended the reaction to include the determination of indium[7] and titanium.[8] Svoboda and Chromý[9–11] have described the use of Xylenol Orange in conjunction with long-chain surface-active agents as a general colour reaction for many metal ions. This particular reaction is different in principle from that described here, in that the purple-red alkaline (pH 10·5) solutions of Xylenol Orange are decolorized by the addition of cationic long-chain quaternary salts, and the addition of metal ions such as calcium, zinc and manganese restores the original reagent colour. Only in a few instances, *e.g.*, with lanthanum, is there a bathochromic shift and production of a new colour body. The formation of micellar aggregates was suggested to be responsible for the changes, although no experimental evidence was presented in support. The mechanism involving the colour change was considered only in terms of a supposed adsorption phenomenon. The authors indicate that the theory is incomplete and they presented the system as a means of determining complexometrically such ions as calcium and magnesium with an indicator which is not normally applicable. The principal disadvantage of this type of system is that it operates in highly alkaline solution where precipitation of many metal ions takes place. Because the reaction involves adsorption, the presence of precipitates will produce interfering effects. Also, this particular reaction was found to be highly susceptible to the effects of several anions.

Reaction mechanism

The importance of micelle production in the formation of ternary complexes was investigated first. The tin(IV)–Catechol Violet–CTAB system was selected for this study as it was the only system which utilized a well defined surfactant.

Preliminary investigations indicated that the presence of micelles is necessary in this type of system because the colour is not formed with quaternary ammonium salts such as tetraethyl- and tetrabutylammonium bromide. These compounds are not surfactants and hence do not produce micelles. In addition, it is known that acid-base indicators in the presence of micelle-forming substances may undergo a change similar to that produced on formation of a ternary complex.[12,13]

To examine the effect of micelle formation it is necessary to determine the critical micelle concentration (CMC) of the surfactant used. (The CMC may be defined as the minimum concentration of surfactant at which micelles are formed.) The simplest and most widely used method uses the marked colour change which occurs in solutions containing surfactant and a suitable dyestuff of opposite charge, when the concentration of surfactant reaches the CMC.[12] This colour change can be observed either visually or instrumentally[13] during the titration.

Eosin and fluorescein have both been used for determining the CMC for cationic surfactants[12] and we have used the closely related dyestuff RBE in view of its previous use.

The CMC was determined in the following manner: an aliquot of RBE was transferred into a 100-ml flask and diluted to about 90 ml. Various amounts of CTAB were added until the range over which the colour change occured was found. This was determined visually to be when the concentration of CTAB was about $4 \times 10^{-6}M$. A series of solutions was then made up in 100-ml flasks with 1 ml of $10^{-4}M$ RBE and 1–5 ml of $10^{-4}M$ CTAB. The absorbances of the diluted solutions were measured at 570 nm (the absorbance maximum of the surfactant–dye salt) in 1-cm cuvettes against a blank containing no CTAB. The results were plotted as the rate of change in absorbance with concentration and are shown in Fig. 1 curve *a*. The curves *b* and *c* were prepared in a similar way, but with 2 ml and 4 ml of $10^{-4}M$ RBE respectively. From these results, it can be seen that the CMC (the point at which dA/dv is maximal) is indeed when the concentration of CTAB is $4 \times 10^{-6}M$.

This procedure was repeated with 2·5 ml of $10^{-4}M$ tin(IV) and 5 ml of $10^{-4}M$ Catechol Violet instead of RBE, *i.e.*, the 1:2 tin–Catechol Violet complex.[5] The solutions were adjusted with sulphuric acid to pH 2, diluted to the mark with distilled water and the absorbances measured at 660 nm. The results (Fig. 2) show that maximum rate of colour change is again obtained at the point at which the CTAB concentration is $4 \times 10^{-6}M$. Thus, it can be seen that the formation of micelles appears to have an important effect on complex formation.

Additional work was carried out with an aqueous acetone medium, which has the effect of raising the CMC. This enables a concentration of CTAB to be used such that the colour change through the CMC is more easily observed. The CMC of CTAB was determined in a similar manner for various concentrations of acetone in water. A 30% v/v acetone–water medium gave a CMC of $10^{-4}M$. As before, the ternary system first began to form appreciably when the concentration of CTAB reached the CMC, *i.e.*, at $10^{-4}M$.

It was noticed that in aqueous acetone media the order of addition of the reagents

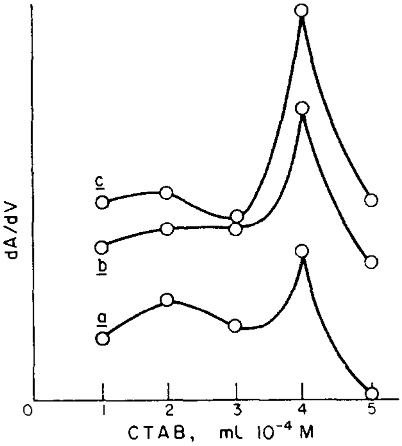

FIG. 1.—Determination of CMC of CTAB with Rose Bengal Extra
(*a*) 1 ml of 10^{-4} Rose Bengal Extra
(*b*) 2 ml of 10^{-4} Rose Bengal Extra
(*c*) 4 ml of 10^{-4} Rose Bengal Extra
All solutions were diluted to 100 ml with distilled water and absorbance measurements were made at 570 nm

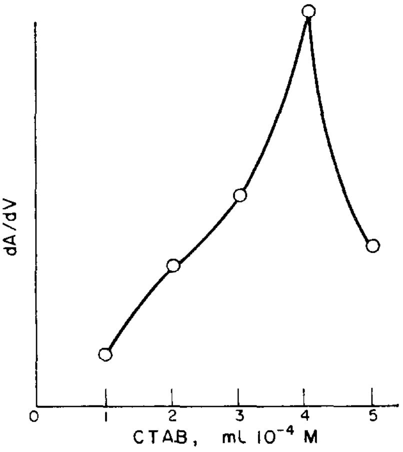

FIG. 2.—Determination of CMC of CTAB with the tin(IV)-Catechol Violet complex. Solutions prepared by diluting 2·5 ml of $10^{-4}M$ Sn(IV), 5 ml of $10^{-4}M$ Catechol Violet, and CTAB (1–5 ml of $10^{-4}M$) at pH 2 with distilled water to 100 ml Absorbance measurements made at 660 nm.

was very important. When the CTAB was added to the tin(IV)-Catechol Violet complex before the acetone (*i.e.*, if the ternary system is formed before the micelles are destroyed by the acetone) the ternary system was not destroyed on subsequent addition of acetone.

The conclusion drawn from this is that it is necessary to form micelles to obtain the system but, once they have been formed, the surfactant concentration can fall below the CMC without unduly affecting the system. Thus, the CMC is also a critical reaction concentration below which little or no complexation occurs.

Further investigations have shown that a number of other elements, namely aluminium, antimony, bismuth, gallium, indium, molybdenum, titanium, tungsten and zirconium undergo similarly controlled colour reactions with Catechol Violet and CTAB.

Nature of complex

The possibility exists that the binary metal–dyestuff chelate could be adsorbed onto the micellar aggregates and the colour change could thus result from interactions with the micelle. Alternatively, the binary chelate could form a true ternary complex with the surfactant in so far as a meaningful whole number of molecules of surfactant might be associated with one molecule of the binary chelate. In the first case the molecular ratio of chelate to surfactant would not be fixed or particularly meaningful.

The molecular ratio of the tin(IV)–Catechol Violet–CTAB system was determined by photometric titration and Job plots to be 1:2:4. The corresponding molybdenum complex of Catechol Violet and CTAB gave a ratio of 1·1:2. It was thus established that these complexes are of definite composition.

It was also found that some of the complexes, *viz.*, with molybdate, tungstate and antimony, can be extracted into organic solvents such as chloroform even if the quaternary ammonium compound is not a surfactant and does not produce a ternary complex in aqueous solution. However, for a given concentration of quaternary ammonium salt, the degree of complex extraction falls with the size of the organic molecule, *i.e.*, the degree of extraction is in the order CTAB > tetrabutylammonium bromide > tetraethylammonium bromide.

The conclusions to be drawn from these results are as follows: the complexes are formed by an ion-association of the quaternary ammonium grouping with the metal–dyestuff chelate. In aqueous solution this only occurs when micelles are formed, that is when a sufficiently high local concentration of the quaternary ammonium grouping is obtained. The extraction of the complexes into organic media may be accomplished in the absence of micelles because the low dielectric constants of the organic media promote the formation of ion-association systems.

It is possible to account for the reaction mechanism of the cation–1,10-phenantholine–anionic dyestuff systems [*e.g.*, $(Ag^+\text{–phen}_2)_2BPR^{2-}$] in a similar manner. Both types of complex exist as finely dispersed precipitates in aqueous solutions and may be extracted into various organic solvents. Furthermore, the colour changes observed with the same dyestuff are very similar in both types of complex. However, in the dyestuff systems it may be the cation–1,10-phenanthroline species which supplies the micelles. This was investigated, as described previously, using the fairly typical 1:2:1 Cu(II)–1,10-phenanthroline–RBE complex.[3] If the Cu(II)–1,10-phenanthroline complex forms micelles, there must be a CMC below which the RBE will not associate with it and, therefore, will not undergo a colour change. However, attempts to determine the CMC in aqueous solution were unsuccessful because if it exists it does so at too low a concentration ($\leqslant 10^{-6}M$) to be detected. This may account for the high sensitivity of this type of reaction.[3]

Nature of colour change

In the light of the information above the following suggestions may be made to explain the colour changes which occur on formation of the ternary complexes.

The colour of triphenylmethane dyestuffs of the type used in this study is due to resonance in the resorcinol portion of the molecule. In general the phenyl group takes little part in the transition.[14] The ternary colour reaction could, therefore, arise from short-range electrostatic interactions involving the charged micelles and the resorcinol part of the dyestuff molecule. Alternatively, and more probably, a charge transfer reaction is responsible for the observed colour changes. The fact that the colour changes observed for different metals with the RBE–1,10-phenanthroline system were virtually identical[3] presents little difficulty since the chromophore of the system is the RBE molecule. Moreover, the metal ion is primarily associated with phenanthroline molecules in a purely co-ordinate bonding arrangement, and is thus unlikely to exert much influence on the RBE molecule. Even if this were not so, and the metal ion were directly bonded to the chromophoric molecule itself, its nature would scarcely effect the colour changes to be expected, as has been discussed elsewhere.[15,16] This is shown by the metal ion-Catechol Violet–CTAB system where the metal ion is directly bonded to the dyestuff through the latter's vicinal hydroxy groups.

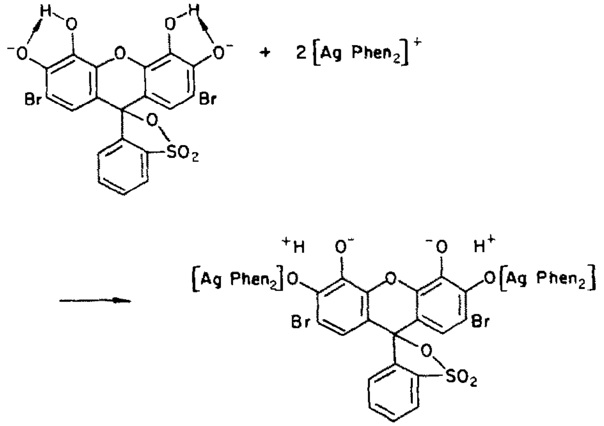

FIG. 3.—Reaction mechanism of silver–1,10-phenanthroline–Bromopyrogallol Red complex.

In the silver–1,10-phenanthroline–Bromopyrogallol Red complex the 560 → 635 nm shift in wavelength of maximum absorption may be explained on the basis that the BPR ion associates with two bisphenanthrolinium silver(I) ions.[1,2] The silver does not react directly with the hydroxy groups of BPR, since no proton release occurs during the reaction. Now the absorption maximum of the fully ionized BPR molecule is *ca.* 630 nm. Apparently, therefore, the association of the two bisphenanthrolinium silver ions produces a change in the BPR molecule which is closely allied to release of the available strongly bonded protons (Fig. 3).

This may be viewed as transfer of an electron from the ionized phenolic groups to the bisphenanthrolinium silver ions, thus weakening the bonding of the last protons. The aromatic chromophore thus assumes a form closely similar to that of the fully ionized BPR molecules. The absence of evidence of proton release does, however, indicate that only a charge transfer is involved, not complete physical removal of the protons. It is also easy to see, therefore, why this bulky uncharged species precipitates from aqueous solution and may be extracted into nitrobenzene.

In the tin(IV)-Catechol Violet-CTAB system it is clear that the cation is initially bonded to the chromophore through the hydroxy groups and that the ion-associating species is the cationic CTAB molecule. Clearly, here, the CTAB cation is unlikely to react with the 1:2 Sn-Catechol Violet chelate at the metal co-ordinating centre and will, therefore, form its ion-association with the binary complex primarily *via* the sulphonic acid group on the phenyl ring. Electrophilic reaction of the quaternary ammonium group at this centre can promote electron-withdrawal from the remaining phenolic groups in the red-purple 1:2 Sn-Catechol Violet complex, along the conjugated bond system as shown in Fig. 4, thus allowing ionization of the remaining protons to produce an absorbing species similar to that of the blue fully ionized Catechol Violet molecule. The resulting ternary complex may further associate with another two CTAB cations to produce an easily precipitated, neutral solvent-extractable species with 1:2:4 molecular proportions of tin, Catechol Violet and CTAB. The scope of this latter type of system, *viz.*, metal-dyestuff-surfactant is large. Many existing spectrophotometric procedures could be adapted to use ternary complexes and so give increased sensitivity of reaction. Furthermore, the use of ternary complexes as indicators in visual titrations should prove very useful and give a more distinct end-point because of the relatively large shift in the wavelengths of maximum absorbance, as demonstrated recently in this laboratory.[17]

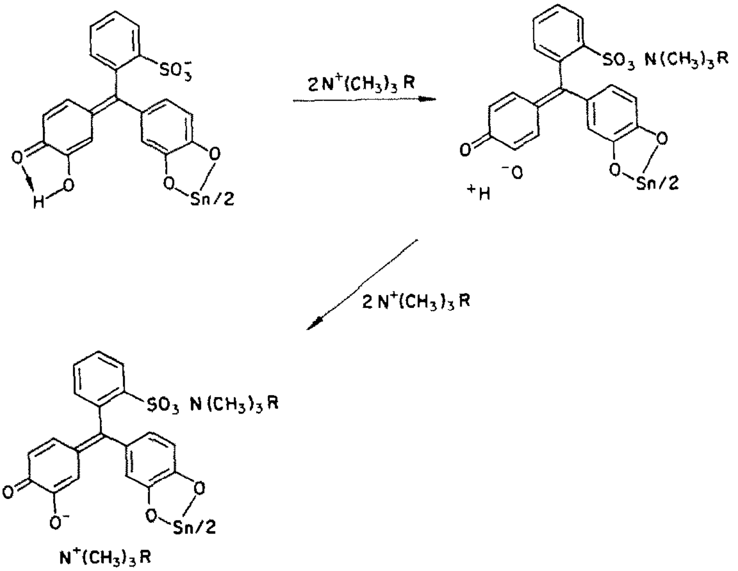

FIG. 4.—Reaction mechanism of tin(IV)-Catechol Violet-cetyltrimethylammonium bromide complex.

Analytical Applications

We have already described the analytical potentiality of the tin(IV)-Catechol Violet colour reaction[5] which may be sensitized by cetyltrimethylammonium bromide to give a molar absorptivity of $95{\cdot}6 \times 10^3$. The utility of this type of reaction may also be demonstrated with the same system for two other elements for which there is a need for sensitive colour reactions, *viz.*, molybdenum and antimony.

Molybdenum

The number of spectrophotometric procedures for the determination of traces of molybdenum is rather limited. Probably the best known and most sensitive is based on the reduction of phosphomolybdic acid to molybdenum blue.[18] However, this frequently gives non-reproducible results and is not generally regarded as satisfactory.

The sensitivities of a few recognised spectrophotometric methods[19] for molybdenum are listed in Table I, together with that for the ternary complex formed with Catechol Violet and cetyltrimethylammonium bromide.

TABLE I.—SENSITIVITIES OF SOME MOLYBDENUM COLOUR REACTIONS

Reagent	Solvent	Molar absorptivity
Thiocyanate	diethyl ether	2×10^4
Toluene-3,4-dithiol	isoamyl alcohol	$1{\cdot}8 \times 10^4$
8-Hydroxyquinoline	chloroform	8×10^3
2-Amino-4-chlorobenzenethiol	chloroform	3.6×10^4
Catechol Violet–CTAB	water	$4{\cdot}6 \times 10^4$

The most recent notable colour reaction devised for molybdenum uses the reagent 2-amino-4-chlorobenzenethiol.[20] However, the water insoluble complex must be extracted into an organic solvent.

Ternary complex characteristics. The addition of CTAB causes a shift in the wavelength of maximum absorption of a solution of ammonium molybdate and Catechol Violet at pH 3–5 from 570 to 675 nm. Catechol Violet alone has an absorbance maximum at 440 nm over the same pH range.

A 2·5-fold molar excess of CTAB and a 1·5-fold molar excess of Catechol Violet over molybdate ensures instantaneous maximum colour development. The order of reagent addition was not found to be important.

The nature of the complex was investigated by continuous variation and slope-ratio plots and corresponded to a molybdenum–Catechol Violet–CTAB ratio of 1:1:2.

Beer's law was obeyed over the range 9·6–96 ppm and the effects of 19 cations and 10 anions are shown in Table II. Only those ions which might be expected to interfere were examined. The major interferences arise from elements which are known to form Catechol Violet complexes, especially those having a normal oxidation state > III. Lead interferes by precipitating the molybdate, and chromate, iron(III), titanium(IV) and vanadate produced turbid solutions. The addition of large molar excesses (*e.g.*, >1000-fold) of indifferent electrolytes also tended to cause some turbidity.

Certain of these elements, *e.g.*, aluminium, zirconium and gallium, could be masked at the 100-fold molar excess level by the addition of a 1000-fold molar excess of fluoride. Aluminium produces a similarly coloured complex though in Table II it appears not to interfere. Iron(III) at this level could also be masked by reduction with ascorbic acid. General masking agents such as EDTA and CDTA broke down the complex. It is possible that a prior solvent extraction of molybdenum (*e.g.*, as the thiocyanate) might result in better selectivity.

TABLE II.—EFFECT OF SOME INTERFERING IONS

Interference	Molar excess relative to Mo	Absorbance at 675 nm	Interference, %
—	—	0·455	—
Al	200	0·460	+1
Bi	100	0·370	−19
Co(II)	100	0·455	0
Cr(III)	100	0·380	−17
Cu(II)	100	0·460	+1
Fe(III)	100	0·355	−22
Ga	10	0·650	+43
In	100	0·490	+8
Mg	100	0·438	−4
Mn	100	0·454	0
Ni	100	0·438	−4
Pb	100	0·040	−91
Sb	100	0·542	+19
Th	100	0·480	6
Ti(IV)	100	0·390	−14
V(VI)	100	0·380	−17
W(VI)	100	0·024	−95
Zn	100	0·438	−4
Zr	100	0·280	−39
Ascorbate	100	0·455	0
Citrate	100	0·381	−16
Chromate	1000	0·275	−39
Cyanide	75	0·463	+2
EDTA	1000	0·124	−73
Fluoride	1000	0·455	0
Oxalate	100	0·420	−8
Tartrate	100	0·456	0
Thiocyanate	1000	0·455	0
Tiron	1000	0·468	+4

Antimony

As with molybdenum, there are few sensitive spectrophotometric methods available for antimony. Perhaps the most sensitive is that between antimony and Bromopyrogallol Red[21] which yields an extinction coefficient of $39{\cdot}2 \times 10^3$ at 560 nm. The method involves measurement of a decrease in absorption at the reagent peak to attain maximum sensitivity. The addition compound formed between hexachloroantimonate(VI) ($SbCl_6^-$) and Rhodamine B also yields good sensitivity ($\varepsilon_{545\ \mathrm{nm}} = 34 \times 10^3$) but involves oxidation to unstable antimony(V) and solvent extraction of the adduct from excess of Rhodamine B.[22]

Ternary complex characteristics. The formation of the antimony–Catechol Violet complex is not accompanied by a distinct colour change as with molybdenum and tin. As observed previously[21] for antimony and Bromopyrogallol Red, the colour reaction consists only of a slight broadening in the absorption spectrum of Catechol Violet. Addition of cetyltrimethylammonium bromide, however, produces a distinct colour change. If the Catechol Violet–CTAB ratio is >1 a blue complex ($\varepsilon_{660\ \mathrm{nm}} = 20 \times 10^3$) is predominantly formed, but if this ratio is <1 a red complex ($\varepsilon_{530\ \mathrm{nm}} = 30 \times 10^3$) is formed.

The optimum pH for maximum colour formation of the red complex was *ca.* 6 and it was found necessary to have at least a 5-fold molar excess of CTAB over Catechol Violet, which in turn must be in at least 2·5-fold excess of the antimony. It was also found possible to use EDTA as a mass masking agent; the addition of a 100-fold molar excess of EDTA reduced the molar absorptivity only to 28×10^3. Under these conditions a linear calibration curve was obtained over the range 6·1–61 ppm of antimony at 530 nm. The interferences in this method were exactly the same as those found by Christopher and West[21] for the Bromopyrogallol Red system, *viz.*, molybdenum, niobium, tungsten, uranium and zirconium. Because of the possibility of two different complexes existing together (*i.e.*, the red and blue complexes) it was not possible to elucidate the ternary complex structure by normal means such as continuous variation plots, *etc.*

However, under carefully controlled conditions the method provides a useful and sensitive reaction for antimony which may be operated in the presence of a wide variety of other metal ions if EDTA is used as masking agent.

EXPERIMENTAL

Reagents

Ammonium molybdate stock solution Dissolve 1·766 g of ammonium heptamolybdate tetrahydrate in 1 litre of distilled water. Dilute as required.

Potassium antimonyl tartrate, $10^{-3}M$. Dissolve 0·3249 g of reagent in 1 litre of distilled water. Dilute as required.

Reagent solution. Prepared by dissolving 0·232 g of Catechol Violet and 1·456 g of cetyltrimethylammonium bromide in 1 litre of distilled water. This solution is *ca.* $6 \times 10^{-4}M$ in Catechol Violet and $4 \times 10^{-3}M$ in CTAB.

Acetate buffer, pH 3·85. Prepared by diluting 114 ml of glacial acetic acid to 1 litre with distilled water and then adjusting the pH to 3·85 with solid sodium acetate (pH meter control).

Acetate buffer, pH 5·8. Prepared by dissolving 20 g of ammonium acetate in distilled water, adjusting the pH to 5·8 with glacial acetic acid (pH meter control) and diluting to 100 ml.

Procedure for calibration curve

Transfer 1–10 ml portions of the 100-fold diluted molybdenum or 10-fold diluted antimony solution, 5 ml of the mixed reagent solution and 10 ml of buffer solution (pH 3·85 for molybdenum; pH 5·8 for antimony) into 100-ml flasks and dilute to volume with water. Measure the absorbance at 675 nm for molybdenum or 530 nm for antimony in a 1-cm cuvette against a reagent blank.

Unknowns should be treated in the same way as solutions used to prepare the calibration curve. EDTA can be used to mask most metal ions in the antimony determination

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Zusammenfassung—Es wird gezeigt, daß die Bildung ternarer Komplexe beim Zusatz oberflachenaktiver Agentien zu verschiedenen Metall-Farbstoff-Chelatsystemen auf Bildung von Mizellen beruhen. Spektrophotometrische Messungen zeigen, daß sich wahre ternare Komplexe mit wohldefinierten Strukturen bilden und daß die beobachtbaren Änderungen in den Absorptionsspektren nicht auf einfache Adsorption des binaren Metall-Farbstoff-Komplexes an mizellare Aggregate zuruckzuführen sind. Es werden einige Vermutungen über die Natur der beobachteten Änderungen geaußert. Die analytischen Moglichkeiten dieser Art Systeme werden verdeutlicht am Beispiel der Bildung solcher Komplexe zwischen Molybdan oder Antimon, Catechinviolett und Cetyltrimethylammoniumbromid, wobei sich molare Extinktionskoeffizienten von $4{,}6 \cdot 10^4$ bzw. $3{,}0 \cdot 10^4$ ergeben.

Résumé—On montre que les complexes ternaires qui se forment lorsqu'on ajoute des agents tensioactifs à divers systèmes chélatés métal-matière colorante dépendent de la formation de micelles. Des mesures spectrophotométriques montrent que des complexes ternaires vrais se forment avec des structures bien définies et que les modifications dans les spectres d'absorption produits ne sont pas dues à une simple adsorption du complexe binaire métal-colorant sur des agrégats micellaires. On présente quelques suggestions pour interpréter la nature des modifications observées. On illustre les possibilités analytiques potentielles de ce type de système par la formation de tels complexes entre le molybdène ou l'antimoine, le violet de catéchol et le bromure de cétyltriméthylammonium, donnant des coefficients d'absorption moléculaire de 4,6 × 10^4 et 3,0 × 10^4 respectivement.

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APPLICATIONS OF ENZYME-CATALYSED REACTIONS IN TRACE ANALYSIS—III

DETERMINATION OF SILVER AND THIOUREA BY THEIR COMBINED INHIBITION OF INVERTASE*

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Summary—Thiourea has been found to enhance the inhibition of invertase by silver ions. The effect is applied to the determination of 1-5 × $10^{-7}M$ silver and of 10^{-7}–$10^{-8}M$ thiourea A mechanism is suggested for the enhancement.

THE ENZYME invertase (β-fructofuranosidease) catalyses the hydrolysis of sucrose into glucose and fructose. The inhibition of the enzyme action by traces of silver(I) and mercury(II) has been applied in the determination of these metals at the 10^{-6} and $10^{-7}M$ levels respectively.[1] Anions that bind strongly with these metals (cyanide, sulphide, iodide, *etc.*) compete with the enzyme for the metal ions, so that the inhibition is diminished. This effect has been used in the determination of $<10^{-7}M$ cyanide or $<10^{-6}M$ sulphide.[2] Numerous other complexing agents such as histidine, methionine and reduced glutathione have also been found to reduce the inhibitory effect of silver.[3] However, of all the metal-binding species that have been examined, thiourea has a unique effect—it enhances the inhibitory effect of silver.[1] This paper describes the application of this effect to the determination of thiourea and of silver at levels lower than those measured previously.[1]

RESULTS

The effect of thiourea on the inhibition of invertase by silver at pH 5·5 is shown in Fig. 1. In the absence of thiourea, there is little inhibition by such small concentrations of silver because of the presence of silver-binding impurities in the enzyme preparation. Yet when $10^{-6}M$ thiourea is present, $10^{-7}M$ silver appreciably inhibits the enzyme, so that analysis for silver at the $10^{-7}M$ level should be possible. Figure 1 also shows the effect of silver plus thiourea on the enzyme at two different concentrations. The relative activity diminishes as the enzyme concentration increases, but proportionately more silver is required to deactivate the larger concentration of enzyme. This indicates that the amount of silver bound by the enzyme is not negligible in comparison with the total amount of silver added, so that the stability and co-ordination number of the enzyme–silver complex cannot be evaluated accurately. However, plots[1] of log $(1 - R.A.)/R.A.$ *vs.* log [Ag^+] (where *R.A.* is the activity of the inhibited enzyme relative to that of the free enzyme under the same conditions), shown in Fig. 2, are

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straight lines with slopes 1·8 and 2·1 for 1 ml and 2 ml of enzyme respectively, showing that about two silver ions are bound by each "site" of the enzyme. Furthermore, the intercepts on the log [Ag^+] axis [= (log $K_{nAg})/n$] are about −6·6 for 1 ml of enzyme, and −6·4 for 2 ml of enzyme, so that when $n = 2$, mean log $K_{2Ag} = -13$. K_{2Ag} is the equilibrium constant for the reaction

$$2Ag^+ + EH \rightleftharpoons Ag_2E^+ + H^+$$

where EH is the enzyme.

The effect of various amounts of thiourea on silver inhibition is given in Fig. 3. Apart from establishing that $>2 \times 10^{-7}M$ thiourea gives maximal enhancement of inhibition by $5 \times 10^{-7}M$ silver, so that $10^{-6}M$ thiourea should be adequate in a method for the determination of silver up to this concentration, it also indicates that it should be possible to develop a method for the determination of $<10^{-7}M$ thiourea on the basis of its enhancement of the inhibition of invertase by silver. Large amounts of thiourea ($>10^{-4}M$) however, reduced inhibition by silver. At pH 4·0, silver had no effect on invertase, whether thiourea was present or not.

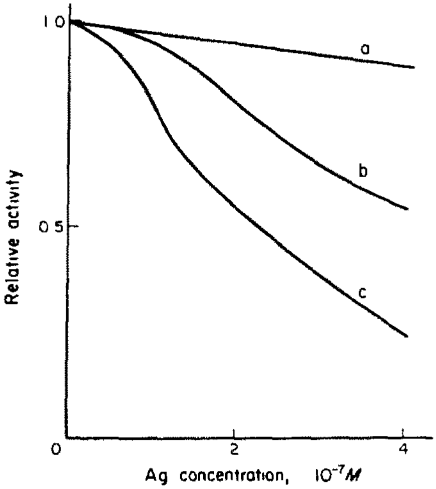


FIG 1.—Inhibition of invertase by Ag^+ at pH 5·5 (*a*) 1 ml of enzyme, no thiourea; (*b*) 2 ml of enzyme, $10^{-6}M$ thiourea, (*c*) 1 ml of enzyme, $10^{-6}M$ thiourea.

Effect of other metals

The effect of $10^{-6}M$ thiourea on the other metal ions known to inhibit invertase was investigated. The results are summarized in Table I. It was also found that $2 \times 10^{-5}M$ thiourea reduced the inhibitory effect of $10^{-7}M$ mercury(II) by 40%. Thus, this concentration of thiourea only reduced or did not affect the inhibitory effect of these ions. Small changes in thiourea concentration at the $10^{-6}M$ level had no effect on the inhibition by silver (Fig. 3). Therefore, unless there is appreciable complexing of thiourea with other metal ions, so that its effective concentration is much reduced, most metals that complex with thiourea will not interfere significantly in the determination of silver. The direct interference of mercury(II) and of large amounts of

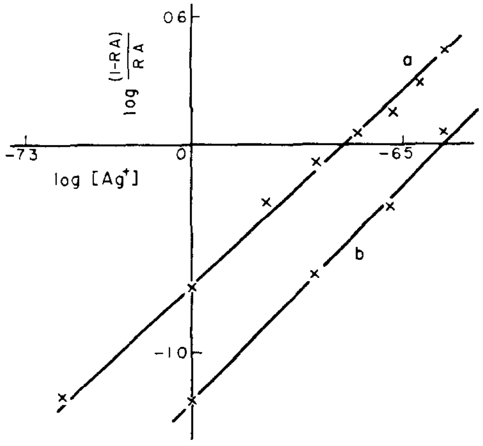


FIG. 2.—Determination of the stability of enzyme-silver complex from the data in Fig. 1. (*a*) 1 ml of enzyme, (*b*) 2 ml of enzyme.

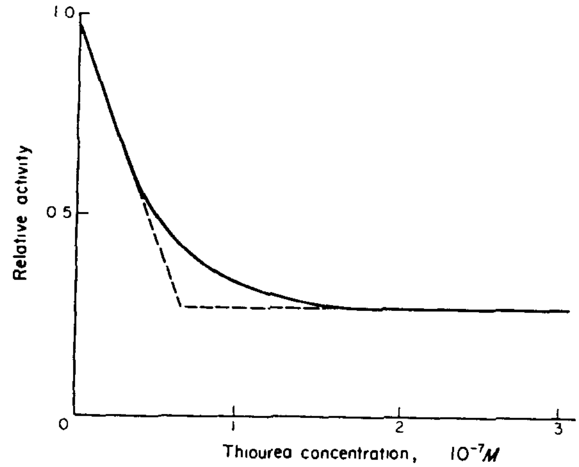


FIG. 3.—Effect of thiourea on the inhibition of invertase by 5 × $10^{-7}M$ Ag^+ at pH 5·5.

TABLE 1.—EFFECT OF CATIONS ON INVERTASE ACTIVITY IN THE PRESENCE OF THIOUREA

Cation	Cu^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	UO_2^{2+}		$[AuCl_4]^-$	
Concentration (*M*)	10^{-5}	5×10^{-3}	5×10^{-4}	$1·4\times10^{-3}$	4×10^{-4}	8×10^{-7}	4×10^{-6}	8×10^{-6}
R.A. (no thiourea)	0·93	0·61	0·68	0·46	0·60	0·80	0·69	0·63
R.A. ($10^{-6}M$ thiourea)	0·95	0·61	0·68	0·46	0·61	0·80	0·69	0·78

common metal ions was eliminated, as in the previous procedure,[1] by adding 1,2-diaminopentanetetra-acetic acid (DPTA) solution to the reaction solution. The relative activity of 1 ml of enzyme solution in the presence of $10^{-6}M$ thiourea and 5 × $10^{-7}M$ silver rose from 0·088 in the absence of DPTA to 0·095 when $10^{-4}M$ DPTA was present, and to 0·350 when the DPTA concentration was 10^{-3}M. The sensitivity in the presence of $10^{-3}M$ DPTA was sufficient to enable 1–5 × $10^{-7}M$ silver to be determined with an error of ±2·5%. The standard deviation for the determination of 10 samples with silver contents ranging from 1·0 to 2·0 × $10^{-7}M$ was 0·28 × $10^{-8}M$. Again, similar concentrations of mercury did not interfere. Four determinations of exactly 2 × $10^{-7}M$ silver in the presence of $10^{-7}M$ mercury(II) gave recoveries of 2·07, 2·00, 2·03 and 2·02 × $10^{-7}M$.

Effect of compounds similar to thiourea

The effect of eight organic compounds with structural or silver-binding similarities to thiourea was measured. Urea, ethylenethiourea, sodium diethyldithiocarbamate, 2-mercaptopyrroline,[4] thiohydantoin, guanylthiourea[5] and dithiobiuret[5] (10^{-6} or $10^{-5}M$) gave $\leq 1\%$ change in the relative activity of invertase in the presence of 5 × $10^{-7}M$ silver. Only thiosemicarbazide ($NH_2.CS.NH.NH_2$) behaved similarly to thiourea. However, it was much less effective. The relative activity was reduced from 0·965 to 0·931 by $10^{-7}M$ thiosemicarbazide and to 0·832 by $10^{-6}M$ thiosemicarbazide, but $10^{-5}M$ thiosemicarbazide restored the relative activity to 0·951.

Determination of thiourea

Very sensitive determination of thiourea in the range up to $10^{-7}M$ was possible by the procedure devised. Results are given in Table II and show the good precision achieved. Interferences were not investigated, but will be those for the determination of silver, *i.e.*, cyanide, sulphide, iodide, gold, large amounts of mercury, *etc.*

TABLE II.—DETERMINATION OF THIOUREA

Taken, $10^{-8}M$	1·0	3·0	5·0	7·0
Found, $10^{-8}M$	0·7	$3{\cdot}0_5$	4·8	7·1
	0·8	$3{\cdot}1_5$	4·8	7·2

$[Ag^+] = 5 \times 10^{-7}M$

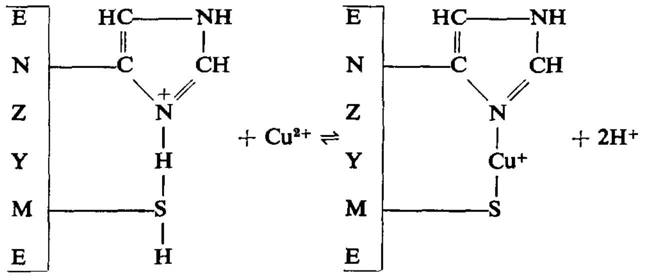
Sulphide reduced the inhibition by 5 × $10^{-7}M$ silver in the presence of $10^{-6}M$ thiourea. The sensitivity to sulphide was slightly greater than of the mercury(II)–invertase system, and the effect could be used for the determination of up to $10^{-7}M$ sulphide by using a procedure similar to that developed with mercury(II)–invertase.[2]

Mechanism of the enhancement

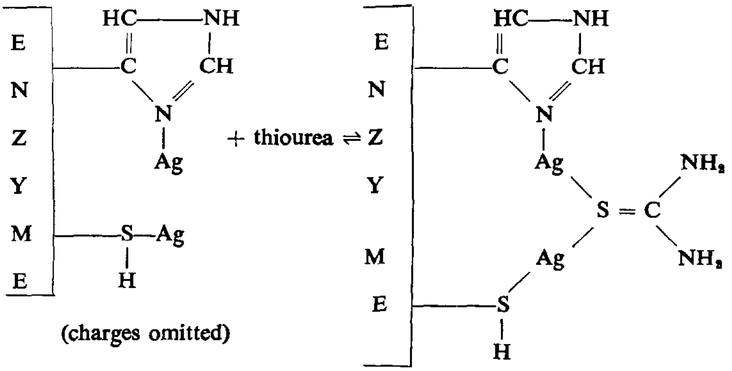
Silver inhibits invertase, in the presence of thiourea, at concentrations *ca.* $10^{-7}M$. When thiourea is absent, this silver is preferentially bound by impurities in the enzyme solution, so that it is not available to inhibit the enzyme. Thus, in the presence of thiourea, it appears that the enzyme binds silver sufficiently strongly to compete with the impurity for the silver ions. This is borne out by the stability constant measurements. It seems that in both instances, two silver ions are bound per active site of the enzyme, but whereas in the absence of thiourea, the enzyme–silver conditional stability constant K_{2Ag} is 1·7 × 10^{-12} mole l^{-1} at pH 5·5, in the presence of an excess of thiourea this has decreased to about 10^{-13} mole l^{-1}. Between these two values must lie the stability constant for the silver–impurity species. Thus, relatively small differences in complex stability seem to be responsible for this effect. The only other compound to show this effect, thiosemicarbazide, forms silver complexes slightly weaker than those with thiourea [β_3 = 12·85 (thiourea) and 12·54 (thiosemicarbazide) at 30°],[6] but it would appear that this small difference is sufficient to reduce markedly the effectiveness of thiosemicarbazide in strengthening the silver–enzyme complex sufficiently to compete successfully with the impurities in silver-binding.

Why is the stability of the enzyme-silver complex increased by the presence of thiourea? Attempts were made to find the ratio of thiourea to silver required for maximal enhancement of inhibition. Extrapolation of the initial part of the curve in Fig. 3 to minimal relative activity (dotted line) gives a value of 1:8 for this ratio. A Job's plot of relative activity *vs.* thiourea and silver concentrations gave a ratio of 1:3. However, it should be remembered that these are the ratios of silver and thiourea added, not of those bound by the enzyme. The stabilities of the enzyme–thiourea–silver, and silver–impurity complexes are such that some of the silver added is not bound by the enzyme. This has been found previously for preparations of brewer's yeast which are virtually free from silver-binding impurities,[7] and thus are sensitive to silver concentrations of the same order as those investigated in the present work. Thus the silver:thiourea ratio could be $\leq 2:1$, which is more reasonable on the basis of the silver-binding properties of thiourea.

The nature of the binding of metal ions by the enzyme has been the subject of some discussion. Each enzyme site binds one copper(II) ion with the displacement of two hydrogen ions; these are considered to come from the imidazole group of histidine, and from a thiol group.[8] The simplest form of this complex-forming reaction can be considered as:



Binding of silver by the enzyme is likely to occur at these same groupings on the enzyme. However, two silver ions are bound in contrast to one copper ion, and the results of Myrbäck[7] imply that only one hydrogen ion is released. The complex with silver can thus be considered as (I). The thiourea could strengthen the complex by forming a bridge between the silver ions to give (II), or a similar structure in which



(charges omitted)

(I) (II)

the thiol group has dissociated. The 2:1 ratio of silver to thiourea would seem to be reasonable in view of the results described above, and the bonding is consistent with that of known silver–thiourea complexes.[5]

EXPERIMENTAL

Chemicals and solutions were as described previously;[1] in addition, a $10^{-5}M$ aqueous thiourea solution is required. Silver nitrate solutions for calibration curves were prepared immediately before use by dilution of $10^{-4}M$ stock solution. All solutions used should be dispensed accurately by pipette.

Determination of silver

Mix in a 10-ml graduated flask $10^{-5}M$ thiourea (1 ml), pH 5·5 buffer solution (1 ml), enzyme solution (2 ml) and sample solution (4 ml, $<8 \times 10^{-7}M$ in silver). Maintain at 30° ± 0·05° for 30 min. Add 50% sucrose solution (2 ml) also at 30°, and measure the optical rotation of the solution after 30·0 min (as described previously).[1] Prepare a calibration graph (optical rotation *vs.* concentration) similarly, using known amounts of silver. When interfering ions are present, add $10^{-2}M$ diaminopentanetetra-acetic acid solution (1 ml) and only 3 ml of sample solution.

Determination of thiourea

Repeat the procedure for the determination of silver but add $10^{-5}M$ silver nitrate solution (1 ml) and sample solution (4 ml) in place of the thiourea and silver solutions.

The effect of thiourea on silver (Fig. 3) was studied by mixing $5 \times 10^{-6}M$ silver solution (1 ml), enzyme (1 ml), pH 5·5 buffer (1 ml), thiourea solutions of various strengths, and diluting to exactly 8 ml with water. After the mixture had been kept at 30° for 30·0 min, 50% sucrose solution (1 ml) at 30° was added, and the optical rotation measured after 30·0 min. The effect of varying the amount of enzyme (Fig. 1) was investigated by a similar procedure involving various silver concentrations and volumes of enzyme solutions (0, 1 or 2 ml), pH 5·5 buffer (1 ml) and $10^{-5}M$ thiourea (1 ml). The effect of thiourea on other metal ions was measured by mixing enzyme solution (1 ml), metal ion solution (1 ml), pH 5·5 buffer solution (1 ml) and diluting to 8 ml, and repeating the procedure above. Likewise the effect of other ligands in place of thiourea was measured by substituting them for thiourea in the procedure for determining thiourea.

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Zusammenfassung—Es wurde gefunden, daß Thioharnstoff die Inhibition von Invertase durch Silberionen verstarkt. Der Effekt wird zur Bestimmung von $1\text{–}5 \, . \, 10^{-7}M$ Silber und $10^{-7}\text{–}10^{-8}M$ Thioharnstoff verwendet. Ein Mechanismus fur die Verstarkung wird vorgeschlagen.

Résumé—On a trouvé que la thiourée exalte l'inhibition de l'invertase par les ions argent. L'influence est appliquée au dosage de l'argent $1\text{–}5 \times 10^{-7}M$ et de la thiourée $10^{-7}\text{–}10^{-8}M$. On suggère un mécanisme pour l'exaltation

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SPECTROPHOTOMETRIC DETERMINATION OF SOME *vic*-DIOLS

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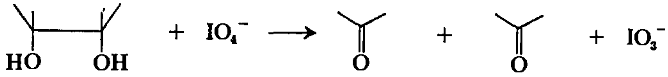
Summary—Conditions have been established for the determination of mannitol and sorbitol (0·4–14 μg), mannose (3·6–18 μg), myoinositol (1·5–6 μg) and pinacol (11–70 μg) by periodate oxidation. The iodate formed is determined spectrophotometrically by reaction with iodide to form tri-iodide. Excess of periodate is masked with molybdate.

The most widely used methods for the determination of *vic*-diols are based on the Malaprade reaction:



Generally, the consumption of periodate is measured by iodimetric titration of the unconsumed periodate.[1] As an appreciable excess of periodate is often necessary for complete reaction within a reasonable time, the resulting difference of two large numbers causes some inaccuracy in the determination. This method is usually applied to mg amounts of *vic*-diols, but recently it was applied to 30–80-μg samples of hexitols, by submicro procedures.[2,3] Formaldehyde and formic acid, the other oxidation products of hexitols, were also titrated consecutively in the same reaction solution.

It would be advantageous to determine directly the iodate formed by the Malaprade reaction. This can be done if the excess of periodate also present is masked with molybdate at pH 3. Under these conditions, only iodate reacts with iodide, so that the iodine formed can be titrated with thiosulphate to give a measure of the iodate concentration.[4,5] This masking reaction has been used to detect 0·1 μg of D-glucose or tartrate,[6] and should readily be applicable to the direct iodimetric titration of *vic*-diols on the submicro scale. The determination of 10^{-6} mole of glycol and glycerol was probably done in this way,[7] but no experimental details are given.

For smaller samples, titrimetric procedures are no longer applicable. Spectrophotometric determination of iodate, however, would be suitable for the analysis of samples of <20 μg. This paper describes the spectrophotometric determination of iodate in the presence of molybdate-masked periodate, and the application of this method to the determination of a range of *vic*-diols.

EXPERIMENTAL

Apparatus

Spectra were recorded on a Unicam SP 800 instrument, and measurements were made on this and on a Beckman DB spectrophotometer.

Solutions

Iodate, 1 00 × $10^{-4}M$ from analytical-grade potassium iodate.
Periodate, $10^{-3}M$ (for hexitols) and $10^{-2}M$ (for other compounds) from sodium metaperiodate
Molybdate, 0·143M from ammonium molybdate.
Iodide, 0 5M from analytical-grade potassium iodide.
Buffer, 0 5M sodium chloroacetate adjusted to pH 3 with dilute hydrochloric acid.

Preparation of calibration curve (and determination of iodate in the presence of periodate)

Into 50-ml graduated flasks transfer 0 5–5-ml portions of the potassium iodate solution and 2 ml of the $10^{-3}M$ or $10^{-2}M$ periodate solution. Add molybdate solution (10 ml) and buffer solution (2 ml) and dilute to *ca.* 35 ml with water. Add the iodide solution (10 ml), and make up to 50 ml with water. Allow to stand for 30 min and measure the absorbance at 350–352 nm in 1-cm cells, against a distilled water blank taken through the whole procedure. Plot absorbance *vs* iodate concentration. For the determination of iodate in the presence of periodate, repeat the procedure for the unknown solution, and read off the iodate concentration from the calibration curve. The periodate concentration should be similar to that of the blank.

Determination of mannitol or sorbitol

Add to a 50-ml graduated flask an aqueous hexitol solution (0·1–1·0 ml, containing 0·4–14 μg of hexitol). Add $10^{-3}M$ periodate solution (2 ml), wash the stem of the flask with sufficient water to bring the volume to 2 5 ml and leave for 20–30 min Add molybdate solution (2 ml) and buffer solution (2 ml) and proceed as for the preparation of the calibration curve. Measure the absorbance in a 1-cm cell *vs.* a water blank taken through the whole procedure, and obtain the concentration of iodate from the calibration curve. The molar concentration of hexitol is then one fifth of that of the iodate found.

Determination of D*-mannose or* D*-glucose*

Add to a 50-ml graduated flask an aqueous hexose solution (0 2–1 ml, containing 3–18 μg of mannose or 3–11 μg of glucose). Add $10^{-2}M$ periodate solution (1 ml) and wash the stem of the flask with sufficient water to bring the volume to 2 5 ml. Add 1 drop of concentrated sulphuric acid, shake, and leave in a water-bath at 45–50° for 1 hr. Cool, add molybdate solution (10 ml), buffer solution (5 ml) and iodide solution (10 ml). Allow to stand for 30 min, and dilute to 50 ml. Measure the absorbance as before to obtain the iodate concentration, which is five times the hexose concentration.

Determination of myoinositol

Add to a 50-ml graduated flask an aqueous solution of myoinositol (0 2–0 7 ml, containing 3–12 μg of the inositol). Add $10^{-2}M$ periodate solution (1 ml), wash the stem of the flask with sufficient water to bring the volume to 2·5 ml, and allow to stand for 2 hr. Add molybdate solution (10 ml) and buffer solution (2 ml). Adjust the volume to *ca* 35 ml with water and add iodide solution (10 ml). Allow to stand for 30 min, make up to 50 ml, and measure as before; the concentration of inositol is one-sixth that of the iodate found.

Determination of pinacol (11–71 μg).

Follow the procedure for the hexoses but, instead of heating, allow to stand at room temperature for 2 hr. The concentration of pinacol is the same as that of the iodate found.

RESULTS AND DISCUSSION

Spectrophotometric determination of iodate in the presence of periodate

The most suitable method for determining iodate was considered to be the spectrophotometric determination of iodine produced by the iodate-iodide reaction. It had already been established[4,5] that hexamolybdoperiodate and molybdate had no effect on the stoichiometry of this reaction at pH 3. Determination of iodine with starch was rejected because of its comparatively high "threshold" value,[8] so two other methods were investigated: spectrophotometric determination of iodine extracted into carbon tetrachloride, or of tri-iodide in the aqueous phase. For the latter a wavelength of 350–352 nm was used rather than 288 nm because of the higher absorbance of molybdate and periodate at the shorter wavelength. The extraction procedure was found to be entirely satisfactory, and had the advantage that iodine was the only absorbing species at the wavelength selected, resulting in lower blank values. However, the determination of tri-iodide in the aqueous phase proved to be equally sensitive ($\epsilon_{350} = 2{\cdot}6 \times 10^4$) and reproducible and was preferred because of its simplicity.

Molybdate and periodate have small absorbances at 350 nm, but do not affect the calibration curve for iodate, in the aqueous solution procedure, provided the blank contains similar amounts of molybdate and periodate. Indeed, the molybdate has a beneficial effect in that it speeds up the iodate–iodide reaction. When this reaction is complete ($<$30 min), the absorbance is stable for at least 2 hr. The absorbances obtained from replicate determinations of various amounts of iodate both in the presence and absence of molybdate and periodate are summarized in Table I. They show that the calibration graphs for iodate are linear and virtually identical. The same results were obtained irrespective of whether the reactions were carried out in darkness or daylight. The blank absorbance increases very slowly in daylight, owing to the decomposition of periodate to iodate, but as this also occurs to the same extent in the sample solutions, there is no change in the net absorbance.

TABLE 1.—DETERMINATION OF IODATE AS TRI-IODIDE

Iodate taken *µmole*	Final absorbance at 350 nm			
	Iodate alone		Iodate + masked periodate*	
	Mean†	Std. devn.	Mean‡	Std. devn.
0·050			0·076	0·001
0·100	0·156	0·010	0·159	0·010
0·200	0·310	0·006	0·314	0·013
0·300	0·467	0·013	0·469	0·012
0·400	0·612	0·008	0·621	0·013
0·500	0·767	0·017	0·774	0·015

* 2 µmole.
† Mean of 5 results.
‡ Mean of 20 results.

The effects of iodide concentration on the absorbance of the final solution are given in Table II. Only when the final iodide concentration was 0·1*M* was constant absorbance obtained. The molar absorptivity at 350 nm under these conditions was $2{\cdot}6 \times 10^4$, which compares well with the value $2{\cdot}64 \times 10^4$ found by previous workers.[9] Calculations based on the association constant for tri-iodide[10] ($\log K = 2{\cdot}9$) indicate that $\geqslant$97% of the iodine will be present as tri-iodide in solutions that are $\geqslant$0·04*M* in iodide, so part of the decrease in the molar absorptivity found for the lower iodide concentrations can be accounted for by incomplete conversion of iodine into tri-iodide. However, the magnitude of the decrease in the presence of higher iodate concentrations is too large to be accounted for in this way, and probably arises from incompleteness of the iodate–iodide reaction under these conditions.

Application to vic*-diols*

The rate of reaction of periodate with *vic*-diols depends on the nature of the compound and the reaction conditions. For instance, hexitols such as mannitol react rapidly, whereas pinacol reacts very slowly. Polyhydroxy compounds often react rapidly with periodate during the early stages of the reaction, but complete oxidation of the products of this initial oxidation is usually slower. The rate of the reaction is also pH-dependent, but the dependency is different for different compounds. For instance, pinacol oxidation is most rapid[11] at pH 3·8 whereas that of glucose increases[12] with increasing pH up to pH 12. Thus it is unlikely that a single set of reaction conditions will be discovered that will be applicable to all types of compound. For this reason, optimum conditions for the determination of various types of *vic*-diol have been established.

TABLE II.—EFFECT OF IODIDE CONCENTRATION ON MOLAR ABSORPTIVITY

Initial [iodate], $10^{-6}M$	Mean ε_{350}		
	$0·003M\ I^-$*	$0·006M\ I^-$†	$0·1M\ I^-$‡
1·00	2·40	2·66	2·55 ± 0·05¶
2·00	2·46	2·61	2·65 ± 0·15
4·00	2·44	2·55	2·61 ± 0·10
6·00	2·41	2·50	2·60 ± 0·07
8·00	2·36	2·46	2·59 ± 0·05
10·00	2·25	2·40	2·58 ± 0·05

* Mean of 4 results.
† Mean of 5 results.
‡ Mean of 20 results.
¶ Standard deviation.

Hexitols. The oxidation of hexitols on the submicro scale (30–80-μg samples) is rapid and stoichiometric,[2] and this was found to be also the case for 1–14-μg samples in unbuffered aqueous media. Experiments with mannitol and sorbitol showed that the reaction, consuming 5 moles of periodate per mole of hexitol, was complete within 20 min and no further reaction occurred within 2 hr. Neither of the reaction products (formic acid and formaldehyde) interfered in any way with the iodate determination. Results for replicate determinations of mannitol and sorbitol are given in Table III. Those for >14 μg of sample are slightly low, probably because

TABLE III —DETERMINATION OF MANNITOL AND SORBITOL

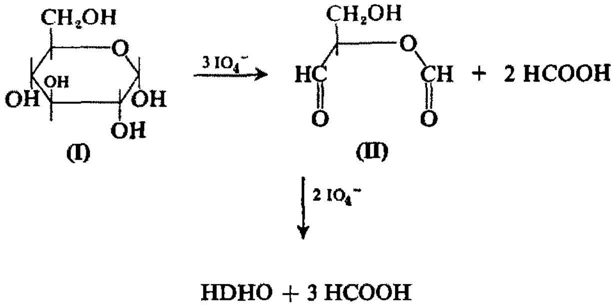
Hexitol taken, μg	Mannitol found, μg			Sorbitol found, μg		
	No. of detns.	Mean	Std. devn.	No of detns.	Mean	Std. devn.
1·82	5	1·94	0·07	3	1·82	0·09
3·64	14	3·82	0·12	6	3·75	0·14
7·28	14	7·37	0·14	6	7·43	0·29
10·9	14	10·8	0·2	6	10·8	0·3
14·6	14	14·4	0·2	6	14·3	0·2
18·2	9	18·0	0·15	3	17·8	0·4
20·0	5	19·8	0·25	2	19·5	

the iodate–iodide reaction is incomplete (see above). Determinations of smaller (0·36–1·8 μg) samples of mannitol, which are summarized in Table IV, are also possible by the same procedure. Suitable modification, *e.g.*, the use of longer-path cells, should enable better accuracy to be obtained with such small samples.

TABLE IV.—DETERMINATION OF SMALLER AMOUNTS OF MANNITOL

Taken, μg	0·36	0·73	1·09	1·46	1·82
Found, μg	0·40 ± 0·02	$0{\cdot}77 \pm 0{\cdot}02_5$	$1{\cdot}14 \pm 0{\cdot}04_5$	1·50 ± 0·05	1·91 ± 0·07
No. of results	2	3	2	2	4

Hexoses. The reaction of periodate with simple aldohexoses takes place in a number of consecutive reactions. Although the complete sequence is not known, the course of the reaction for α-D-glucopyranose (I) can be summarized as follows:



Consumption of the first two moles of periodate is rapid, but the uptake of each of the further three moles of periodate becomes increasingly slow, because of the slower reaction of periodate with the reaction products,[14] such as β-formylglyceraldehyde (II). Furthermore, as *ca.* 15% of glucose is in acyclic and furanose forms, these isomers rapidly consume a mole of periodate during the fission of the C_5—C_6 bond.[15] These facts indicated that it was unlikely that satisfactory results for the determination of aldohexoses would be possible unless complete oxidation, with the consumption of five moles of periodate, could be achieved.

The rate of production of iodate by oxidation of glucose with periodate, under the experimental conditions used for the determination of hexitols, is depicted in Fig. 1, in which it is seen that the rate falls off after two moles of iodate have been produced per mole of glucose present, and that only after 21 hr have five moles of iodate been formed. Mannose reacted similarly, but a little more rapidly. Thus it was necessary to increase the reaction rate to attain complete reaction in a reasonable time. Although this could have been done by raising the pH to 12, it was also found that the reaction rate was appreciably higher in 0·5*M* sulphuric acid. Complete reaction of 10 μg of glucose was attained in an hour by the combined modification of adding a drop of concentrated sulphuric acid to the reaction mixture, increasing the periodate concentration five-fold, and raising the reaction temperature to 45–50°. Table V gives the results of analysis of D-mannose and D-glucose under these conditions. Accurate results were obtained for 3·6–18·0 μg of mannose and for 3·6–10·8 μg of glucose. Reaction is incomplete for larger amounts of glucose.

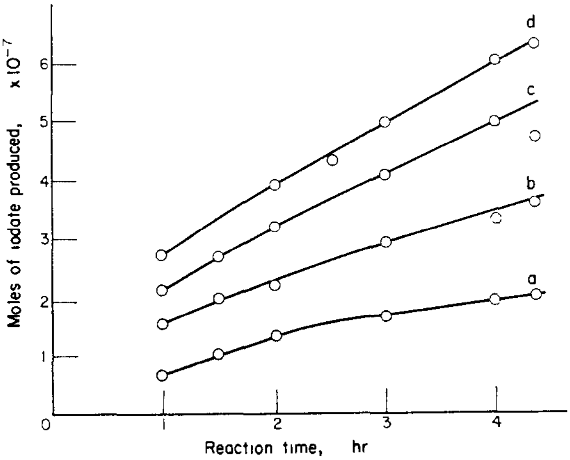


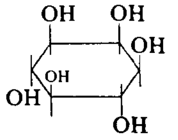
Fig. 1.—Rate of iodate production by the oxidation of (*a*) $0 5 \times 10^{-7}$; (*b*) 10^{-7}; (*c*) $1{\cdot}5 \times 10^{-7}$; (*d*) 2×10^{-7} mole of D-glucose with 2×10^{-6} mole of periodate using the procedure for determining hexitols. Iodate produced after 21 hr was (*a*) $2 6 \times 10^{-7}$; (*b*) $5{\cdot}2 \times 10^{-7}$; (*c*) $7{\cdot}4 \times 10^{-7}$ mole.

Table V.—Determination of glucose and mannose

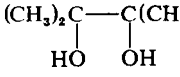
Hexose taken, *μg*	3 6	7 2	10 8	14 4	18 0
Glucose found, *μg**	3 6 ± 0 2 (7)	7·1 ± 0 3 (7)	10 5 ± 0 3_5 (4)	13·7 ± 0 4 (4)	16·9 (3)
Mannose found, *μg**	3 8 ± 0 2 (6)	7 3 ± 0 2 (6)	11 0 ± 0 2 (4)	14 4 ± 0 3 (5)	18 2 ± 0·2 (2)

* Mean result ± std. dev. (no. of determinations).

Myoinositol. This compound (III) reacted very slowly under the conditions used for the determination of the hexitols: 2 days were required for the consumption of



(III)



$$\underset{\text{HO}}{(\text{CH}_3)_2\text{C}}\text{—}\underset{\text{OH}}{\text{C}(\text{CH}_3)_2}$$

(IV)

ca. 6 moles of periodate per mole of inositol. However a five-fold increase in the periodate concentration brought the reaction time down to reasonable proportions The effect of time on the reaction under these conditions is summarized in Table VI. In all cases, more than six moles of periodate were consumed—up to 6·8 moles in the experiment with the smallest inositol concentration—if the reaction was allowed

Table VI —Rate of reaction of myoinositol with periodate

Myoinositol taken, *μmole*	Moles of iodate produced per mole of myoinositol after			
	1·5 hr	2 hr	2 5 hr	4 5 hr
0·34	5 4	6 2	6 2	6 8
0 68	5 4	6 0	6 1	6 5
1 02	5 3	5 8	6 1	7 0
1 36	5 3	5 8	6 1	6 3
1 70		5 4	6 1	6·3

to proceed for some hours. This is in agreement with the results of other workers for larger amounts of inositol.[2,16] However, if the reaction was stopped after *ca.* 2 hr, it was possible to obtain reasonably accurate recoveries of myoinositol on the basis of the consumption of 6 moles of periodate. Results obtained in this way are given in Table VII.

TABLE VII.—DETERMINATION OF MYOINOSITOL

Taken, μg	3·06	6·12	9·2	12·2
Found, μg*	3·02 ± 0·25	5·94 ± 0·25	8·9 ± 0·4	11·7 ± 0·5

* Mean value ± std. devn. (7 variates).

Pinacol. The oxidation of pinacol (IV) by periodate is slow, most probably because the formation of the cyclic ester between these compounds is hindered.[13,17] Indeed, in unbuffered aqueous solution, with the hexitol determination conditions, no measurable oxidation of pinacol had occurred after 2 days. However, oxidation of pinacol is fastest[17] at pH 1. Addition of a drop of concentrated sulphuric acid to the reaction medium, and a five-fold increase in periodate concentration gave quantitative oxidation (consuming one mole of periodate per mole of pinacol) within 2 hr. The amount of iodate produced did not change for at least another 2 hr, either in darkness or daylight. Results obtained for the determination of (11–71 μg) of pinacol under these conditions are given in Table VIII. The method of addition of acid is not critical. Addition of a larger volume of more dilute acid gave identical results.

TABLE VIII.—DETERMINATION OF PINACOL

Taken, μg	11·8	23·6	35·4	47·2	59·0	70·8
Found, μg*	12·5 ± 0·8 (7)	24·1 ± 0·9 (7)	35·4 ± 1·1 (7)	47·1 ± 1·2 (8)	57·7 ± 0·8 (6)	70·1 (2)

* Mean result ± std. devn. (no. of determinations).

Conclusion

Many of the compounds investigated were oxidized completely by periodate within 2 hr only when at least a 100-fold excess of periodate was used. The determination of the amount of periodate consumed under these circumstances is almost impossible, whereas the determination of the iodate produced can be done simply, rapidly, accurately and without interference.

The various conditions described for the determination of the different types of *vic*-diols should be suitable for the determination of most other *vic*-diols and other compounds that are oxidized by periodate. An appropriate procedure should be selected in accordance with the rate of oxidation of the compound. However, if a universal procedure for any *vic*-diol is required, the method devised for the hexoses is most likely to be suitable. However, under these more vigorous conditions, periodate oxidizes compounds that are normally resistant to it, so that the determination of readily oxidized species in the presence of these normally inert compounds, such as tartrate in the presence of citrate, is vitiated. This will be described in a future paper.[18]

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Zusammenfassung—Die Bedingungen zur Bestimmung von Mannit und Sorbit (0,4–14 μg), Mannose (3,6–18 μg), Myoinosit (1,5–6 μg) und Pinacol (11–70 μg) durch Perjodatoxidation wurden entwickelt. Das gebildete Jodat wird spektrophotometrisch durch Reaktion mit Jodid zu Trijodid bestimmt. Überschussiges Perjodat wird mit Molybdat maskiert.

Résumé—On a établi des conditions pour la détermination des mannitol et sorbitol (0,4–14 μg), mannose (3,6–18 μg), myoinositol (1,5–6 μg) et pinacol (11–70 μg) par oxydation periodique. On dose l'iodate formé spectrophotométriquement par réaction avec l'iodure, formant du triiodure. L'excès de periodate est dissimulé au moyen de molybdate.

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GRAVIMETRIC DETERMINATION OF NICKEL WITH QUINOXALINE-2,3-DITHIOL BY PRECIPITATION FROM HOMOGENEOUS SOLUTION

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Summary—The investigation of quinoxaline-2,3-dithiol as a gravimetric reagent for nickel is described A derivative of the dithiol, *S*-2-(3-mercaptoquinoxalinyl)thiuronium chloride is used as a generating agent in a PFHS method because of its relative stability and solubility in aqueous ethanol Nickel, 2 5–25 0 mg, can be precipitated at pH 2–3 as $(C_8H_5N_2S_2)_2Ni$. After filtration the precipitates are washed first with aqueous ethanol to remove traces of absorbed reagent and then with benzene to remove a small amount of decomposition product of the reagent, the characterization of which is described. The precipitates are stable and can be dried in air at 110–120°. Errors of less than 0·15% are obtained in the analysis of solutions containing 25 mg of nickel. The selectivity of the reagent is discussed and some suggestions are made for masking the interference of other elements.

SEVERAL methods have been proposed for the determination of nickel by precipitation from homogeneous solution (PFHS). The reactions employed include direct synthesis of the reagent, complexation and replacement, volatilization of solvents, and various pH effects. These methods have been summarized in recent reviews.[1,2] Various dioximes, particularly dimethylglyoxime, are still the most widely used reagents for the determination of nickel but so far ligands containing sulphur as the donor atom have not been so employed. This may be due to the generally recognized instability of sulphur compounds as reagents. However, as nickel(II) shows considerable affinity towards sulphur compounds, it is useful to explore the use of stable derivatives of such compounds for the slow "*in situ*" generation of the reagents.

The reagent *S*-2-(3-mercaptoquinoxalinyl)thiuronium chloride (MQT) has already been used for the spectrophotometric determination of cobalt and nickel.[3] This paper reports an extension of the use of MQT in the determination of larger amounts of nickel. In weakly acidic solutions MQT hydrolyses slowly to form quinoxaline-2,3-dithiol (QDT) and nickel is precipitated as the blue-black complex $(C_8H_5N_2S_2)_2Ni$. The complex can be isolated easily in pure form and is non-hygroscopic and thermally stable. The gravimetric (PFHS) method for nickel described here has been based on these observations.

EXPERIMENTAL

Reaction of reagent with nickel

Nickel(II) reacts with QDT in alkaline solution to give a soluble red complex. On acidification of this solution, or on addition of QDT to an acid solution of nickel(II), an insoluble dark coloured complex is formed.

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Initial studies with QDT as a gravimetric reagent were unsuccessful because of the limited solubility of the ligand in common solvents and the pronounced instability of both the solid reagent and any solutions. Moreover, the precipitates formed by direct reaction of nickel with QDT were extremely difficult to filter. The use of the PFHS method with MQT as a generating agent was therefore investigated.

Studies were undertaken to determine the MQT concentration, solvent composition, temperature, reaction time and pH of solution which would result in the formation of a pure, easily filterable precipitate and quantitative recovery of nickel.

The optimum conditions found were:

(*i*) addition of sufficient reagent to provide a 3–4 molar excess of MQT over nickel,
(*ii*) use of 50% v/v aqueous ethanol as solvent,
(*iii*) heating the solution for up to 3 hr at about 60° (steam-bath temperature),
(*iv*) precipitation in unbuffered solutions to allow the initial pH of the reagent solution to change in the course of reaction (see Table I).

TABLE I.—RECOVERY OF NICKEL IN THE PRESENCE OF A 3·5 MOLAR-EXCESS OF MQT AS A FUNCTION OF TIME, SHOWING THE CHANGES IN pH IN UNBUFFERED SOLUTION DURING PFHS

Time, *min*	pH at 20°C	Recovery of nickel, %
0	5·3	0
5	3·4	0
10	1·2	11·1*
15	2·2	20·0
30	2·4	52·4
60	2·5	85·5
90	2·8	99·8†
120	2·8	99·8†
180	2·9	99·9†

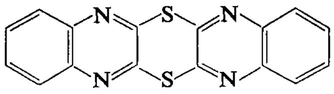
* Solution becomes dark green.
† No nickel detected in the filtrate.

It was found that the extent and speed of hydrolysis of MQT to QDT is increased by increase in pH, but that the optimum pH for complete precipitation of the nickel complex lies between 2 and 3. Hydrolysis at fixed pH values of 3 or 4 appears to be too slow and incomplete and a higher initial pH is necessary. The use of unbuffered solutions thus proved necessary.

The precipitates formed under these conditions could be filtered off quickly and easily. They did not "creep" nor adhere to the walls of a beaker, provided that clean and unscratched beakers were used.

After filtration through a porosity 4 sintered glass crucible the precipitate was washed with 50% aqueous ethanol, acidified with hydrochloric acid to about pH 3, to remove the excess of undecomposed reagent. However the material still remained contaminated with a decomposition product of the reagent and small positive errors were obtained. The contamination can be completely removed by several washes with small portions of hot benzene.

The benzene-soluble impurity was isolated as yellow needle-like crystals subliming above 300°. This was confirmed by differential scanning calorimetry (DSC). The elemental analysis of the compound suggested the empirical formula $C_8H_4N_2S$; however the mass spectrometric determination of the molecular weight indicated a dimer of possible formula



Taeger and El-Hewehi[4] have reported the isolation of a monomer with this empirical formula, as a by-product of the alkaline hydrolysis ofMQT, and described it as brown needles, m.p. 235° (decomp.).

Investigation of the weighing form

Thermogravimetric analysis (TGA) of the blue-black precipitate showed that there was no loss of weight on heating up to 325°. Above this temperature there was a rapid loss of weight and at about 1000° the weight of the residue agreed with the calculated amount of nickel(II) oxide.

Differential scanning calorimetry confirmed that the precipitate underwent exothermal decomposition above 325°. The results of thermal analysis are shown in Fig. 1.

Elemental analysis of the blue-black material gave C, 43·1%; H, 2·2%; N, 12·7%; S, 28·8%; Ni, 13·1%; $(C_8H_6N_2S_2)_2Ni$ requires C, 43·15%; H, 2·3%; N, 12·6%; S, 28·8%; Ni, 13·2%.

The molecular weight of the material could not be determined by the conventional methods because of the insolubility in any of the common organic solvents. The solid material was not sufficiently volatile to give any mass spectra at temperatures of up to 350°. Magnetic measurements at room temperature showed that the compound was diamagnetic and thus possibly contained square-planar nickel(II). Since the composition of the blue-black material indicated the presence of two more hydrogen atoms than in the red soluble complex previously reported,[3] it is suggested that the two compounds are related in the following way

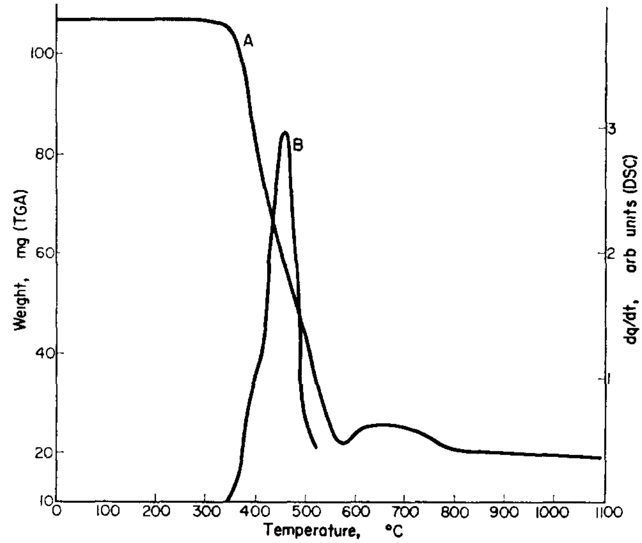
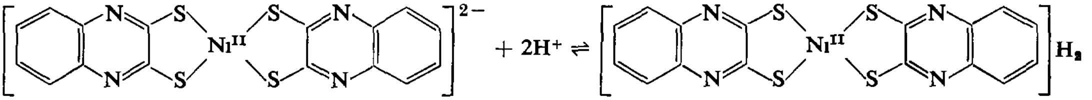


Fig. 1.—Thermal analysis of nickel-QDT complex
A—Thermogravimetric analysis
B—Differential scanning calorimetry



I. Red, anionic. II. Blue-black, neutral.

The neutral compound dissolved in alkalis to give a solution containing the red species I. There was also an indication of a green compound in solution at low values of pH (see Table I). The blue-black solid dissolved in concentrated sulphuric acid to give a green solution. The existence of three such nickel-QDT complexes has been reported by Stevančević.[5] The empirical formula corresponding to II has been adopted for the weighing form in the gravimetric method.

The exact position of the two additional hydrogen atoms is at present uncertain; they may be associated with the quinoxaline nitrogen atoms. The general properties of this material are indicative of a polymeric structure.

Reagents

S-2-(3-*mercaptoquinoxalinyl*)*thiuronium chloride solution*. An approx. 0·5% w/v solution of MQT freshly prepared in 50% v/v aqueous ethanol. The MQT is made as described previously.[3]

Standard solution of nickel. Prepared from analytical-grade nickel(II) ammonium sulphate hexahydrate and standardized gravimetrically with dimethylglyoxime.[6]

Procedure

Add an aliquot of nickel solution to sufficient reagent solution, in a beaker, to make the molar ratio of MQT to nickel approximately 3·5. Adjust the volume with ethanol and/or water to give a final solution that contains 50% of alcohol by volume (note 1). Cover the beaker with a watch-glass and heat on a steam-bath for about 3 hr (note 2). Filter the hot solution through a porosity 4 sintered glass crucible, washing the precipitate with about 100 ml of 50% v/v aqueous ethanol acidified with hydrochloric acid to about pH 3, and then with about 75 ml of hot benzene in small portions. Dry for 1 hr at 110–120° and weigh as $(C_8H_5N_2S_2)_2Ni$ which contains 13·18% of nickel.

Notes

1. The nickel solution should be neutral or weakly acidic. For between 2·5 and 25·0 mg of nickel a final volume of 200 ml is satisfactory.
2. Precipitation is complete when the colour of the supernatant solution has changed from green to orange-yellow. The reaction time is dependent on the amount of nickel present and on the MQT/nickel ratio.

RESULTS AND DISCUSSION

Analysis of standard solutions by the recommended procedure showed coefficients of variation for the determination of about 2·5 and 25 mg of nickel to be 0·90% and 0·13%, respectively. The results of analysis are summarized in Table II.

TABLE II.—RESULTS OF REPLICATE DETERMINATIONS OF NICKEL

Added, *mg*	Found,* *mg*	
	Mean	Standard error
2·55	2·55	0·010
6·38	6·43	0·026
12·76	12·79	0·018
25·52	25·53	0·013

* Mean and standard error for 6 variates.

A preliminary study of interferences showed that a number of metallic ions precipitate under the conditions described for nickel. Burke and Yoe[7] and Ayres and Annand,[8] who utilized the formation of the blue nickel–QDT complex in absorptiometric methods, reported interference from Cu(II), Fe(III), Pt(IV), Pd(II) and Ag(I). The present work has confirmed this and also shown that interference occurs in the presence of Co(II), Mo(VI), W(VI), Zn(II) and Pb(II).

Errors of less than 1% were obtained, however, in the determination of about 12·5 mg of nickel in the presence of a 100-fold excess of NH_4^+, Na, K and Mn(II) and a 50-fold excess of Mg(II). Presence of about 12·5 mg of Fe(III) or Cr(III) could be tolerated if excess of citric acid were added, but the precipitation reaction took about 4 hr. A 100-fold excess of the following anions can be tolerated: chloride, sulphate, nitrate, thiocyanate and citrate. Tartrate and EDTA interfere and must be absent. Substances which increase the pH by hydrolysis, *e.g.*, salts of strong bases and weak acids, generally interfere and should be absent.

MQT is at least as accurate and precise a reagent as dimethylglyoxime for the gravimetric determination of nickel. Both reagents produce precipitates which have the good filterability normally associated with the PFHS method. MQT has already been shown to be a more efficient absorptiometric reagent for nickel than dimethylglyoxime,[3] thus it is an attractive single reagent for the determination of nickel over a wide range of concentrations, provided that its lower selectivity can be tolerated.

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Zusammenfassung—Die Untersuchung von Chinoxalin-2,3-dithiol als gravimetrisches Reagens für Nickel wird beschrieben. Ein Derivat des Dithiols, S-2-(3-Mercaptochinoxalinyl) thiuroniumchlorid wird als Dithiolquelle in einer homogenen Fällungsmethode verwendet, da es in waßrigem Äthanol relativ stabil und löslich ist. 2,5–25,0 mg Nickel können bei pH 2–3 als $(C_8H_5N_2S_2)_2Ni$ gefällt werden. Nach der Filtration werden die Niederschläge zuerst mit waßrigem Äthanol gewaschen, um Spuren von adsorbiertem Reagens zu entfernen, dann mit Benzol, um eine kleine Menge Zersetzungsprodukt des Reagens zu entfernen, dessen Charakterisierung beschrieben wird. Die Niederschläge sind stabil und können bei 110–120° an der Luft getrocknet werden. Bei der Analyse von Lösungen mit 25 mg Nickel erhält man Fehler unter 0,15%. Die Selektivität des Reagens wird diskutiert und einige Vorschläge zur Maskierung der Störungen von anderen Elementen gemacht.

Résumé—On décrit l'étude du quinoxaline 2,3-dithiol comme réactif gravimétrique du nickel Un dérivé du dithiol, le chlorure de S-2-(3-mercaptoquinoxalinyl) thiouronium est utilisé comme agent générateur dans une méthode de précipitation en phase homogène par suite de sa stabilité relative et de sa solubilité en éthanol aqueux. On peut précipiter 2,5–25,0 mg de nickel à pH 2–3 à l'état $(C_8H_5N_2S_2)_2Ni$ Après filtration, on lave les précipités d'abord à l'éthanol aqueux pour éliminer des traces de réactif adsorbé puis au benzène pour éliminer une petite quantité de produit de décomposition du réactif, dont on décrit la caractérisation. Les précipités sont stables et peuvent être séchés à 110–120°. On obtient des erreurs de moins de 0,15% dans l'analyse de solutions contenant 25 mg de nickel. On discute de la sélectivité du réactif et fournit quelques suggestions pour la dissimulation de l'interférence d'autres éléments.

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DETERMINATION OF ALUMINIUM IN PLUTONIUM METAL BY DIFFERENTIAL LINEAR SWEEP OSCILLOGRAPHIC POLAROGRAPHY*

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Summary—A procedure has been developed for the polarographic determination of aluminium in plutonium. The plutonium is separated by anion-exchange in a nitrate medium, and the aluminium is determined in the eluate by use of Superchrome Garnet Y. The aluminium concentration range in the polarographed solutions is 0·020–0·800 μg/ml. The average recovery of aluminium was 99·3%, relative standard deviation 7·2%. Of 20 common impurities found in plutonium metal, only molybdenum and titanium cause significant interference; both can be removed by ion-exchange.

The half-wave potential of aluminium is very electronegative and is preceded by the hydrogen wave. This causes major problems in the direct polarographic determination of aluminium.[1] A method for avoiding this problem was developed by Willard and Dean.[2] It is based on the change in the polarographic behaviour of a dye after it forms a complex with aluminium. The dye used to form the complex was Pontachrome Violet SW(C.I. 169). The dye-aluminium complex has been investigated further at the dropping mercury electrode,[3,4] and Florence *et al.*[5] investigated the oxidation of the complex at the rotating pyrolytic graphite electrode. Adcock[6] used the dye Superchrome Garnet Y, SGY(C.I. 168), for the determination of aluminium. SGY has greater solubility than Pontachrome Violet SW. Since the work of Adcock, a number of papers have appeared on the aluminium–SGY complex and on the determination of aluminium by using the reduction of the aluminium–SGY complex.[7–11]

This paper reports a polarographic method for the determination of aluminium in plutonium metal by using anion-exchange for preliminary separation of plutonium, and then reduction of the aluminium–SGY complex.

EXPERIMENTAL

Apparatus

A Davis Differential Cathode Ray Polarotrace, Type A-1660 (Southern Analytical, Ltd., Camberley, England) equipped with an electrode stand and a constant-temperature water-bath, was used. All polarographic measurements were made at 25·0 ±0·1°. A polarographic cell with a mercury pool anode was used throughout the investigations. Dual 15-cm long capillaries were used for all measurements. The $m^{2/3}t^{1/6}$ value, obtained at zero voltage in a buffer solution with a $1{\cdot}5 \times 10^{-4}M$ SGY concentration was 2·12.

The pH values of the solutions were measured with a Beckman Model 76 Expanded Scale pH Meter and a glass electrode. The pH was adjusted with hydrochloric acid or ammonium hydroxide.

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Reagents

The sodium salt of Superchrome Garnet Y(SGY) was obtained from Keystone Aniline and Chemical Company (Chicago, U.S.A.) The dye was purified by a double recrystallization from ethanol, and a $3{\cdot}75 \times 10^{-3}M$ solution was prepared by dissolving the proper quantity of the dye in water.

The ammonium acetate buffer solution was prepared by mixing 250 ml of $1{\cdot}0M$ ammonium acetate solution, 250 ml of $1{\cdot}0M$ ammonia solution and 500 ml of $1{\cdot}0M$ hydrochloric acid. The pH of this solution was then adjusted to a value of 3·40 ± 0·20.

The anion-exchange resin, Dowex 1 × 2, was prepared according to Kressin and Waterbury.[12] All other chemicals were reagent grade, and the solutions were prepared in the normal manner.

Safety precautions

Extreme care must be exercised in the handling of plutonium because of its toxicity. All work with plutonium was performed in a glove-box. The solutions containing the separated aluminium were analysed polarographically under a well-ventilated hood.

Procedure for sample preparation

A weight of plutonium metal was selected so that 1–50 μg of aluminium were present. This was dissolved in a 150-ml beaker with a minimum volume of $3M$ hydrochloric acid. Then 15 ml of concentrated nitric acid were added, and the solution was evaporated to incipient dryness under an infrared lamp. The beaker and watch-glass were washed with $7{\cdot}2M$ nitric acid, and then 1 ml of 30% hydrogen peroxide was added. The solution was warmed on a hot-plate for 5 min. A change to green in the colour of the solution indicated that the plutonium had been oxidized to plutonium(IV). The beaker walls and cover-glass were washed with a minimum volume of $7{\cdot}2M$ nitric acid, 10 g of the anion-exchange resin were added to the beaker, and the mixture was stirred for about 10 min. The slurry was transferred to a column which contained an additional 10 g of anion-exchange resin. The flow through the column was adjusted to 10 ml/min, and the column was washed with 100 ml of $7{\cdot}2M$ nitric acid. The eluate, which contained the aluminium, was collected in a 150-ml beaker.

The 150-ml beaker was placed under an infrared lamp, and the solution was evaporated to incipient dryness. The beaker and watch-glass were then washed with a minimum volume of water. The pH of this solution was adjusted to 3·40 ± 0·20 and the solution was transferred to a 50-ml volumetric flask; 10 ml of ammonium acetate buffer were added, followed by 2 ml of SGY stock solution. The volumetric flask was placed in a water-bath for 15 min at 75° to hasten the complete formation of the aluminium–SGY complex. The solution was cooled and diluted to volume with water, and a 5-ml portion was transferred to the electrolysis cell. The solution was purged of oxygen by passing purified nitrogen gas through the solution for 15 min. The peak current was read at −0·510 V *vs.* Hg pool

Calibration procedure

A calibration curve for aluminium was prepared by transferring an appropriate portion of a standard aluminium solution into a 150-ml beaker containing 10–15 ml of $7{\cdot}2M$ nitric acid, adding 10 g of the anion-exchange resin, and following the procedure described above. Twenty-eight aluminium solutions, of seven different concentrations, were prepared and polarographed. The mean results are given in Table I and show that the peak current is proportional to the aluminium concentration at pH 3·40. The average relative standard deviation for all polarograms at all concentrations was 7·2%.

TABLE I.—PEAK CURRENT AS A FUNCTION OF THE ALUMINIUM CONCENTRATION AT pH 3·40 ± 0·20

[Al], $\mu g/50\ ml$	i_p μA	$i_p/[Al]$ $\mu A/\mu g/ml$
1·00	0·022	1·10
2·50	0·057	1·15
5·00	0·109	1·09
10·0	0·245	1·23
20·0	0·501	1·25
40·0	0·981	1·23
60·0	1·39	1·16

RESULTS AND DISCUSSION

The effect of pH on the diffusion current was examined, using 1·5 × $10^{-4}M$ SGY solutions which contained 0·400 μg of aluminium and 0·2 ml of the ammonium acetate buffer per ml. The influence of pH on the diffusion current is apparent if the diffusion current is plotted *vs.* pH (Fig. 1). The rounded maximum of the curve is at pH 3·4. If the pH is maintained at this value ±0·20, the error due to pH variation would be less than 1%.

The effect of the concentration of SGY on the diffusion current was examined with solutions which contained 0·400 μg of aluminium and 0·2 ml of the ammonium acetate buffer per ml at pH 3·40 ± 0·20, and various amounts of SGY.

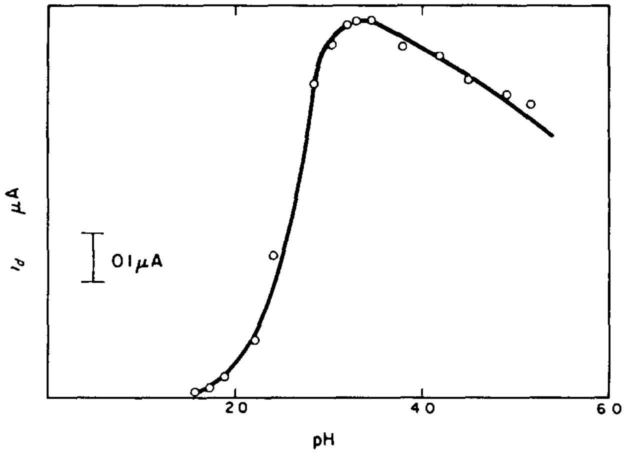

Fig. 1.—Variation of the diffusion current with pH.
Aluminium, 0·400 μg/ml; SGY 1·5 × $10^{-4}M$; acetate buffer 0·2 ml/ml.

The influence of the SGY concentration is shown in Fig. 2, where the diffusion current is plotted *vs.* SGY concentration. An SGY concentration of 1·5 × $10^{-4}M$, in the middle of the narrow flat maximum, was selected for use.

To be certain that all the aluminium had been complexed, the solutions were heated to 75° in a water-bath. It was found that heating the solutions to this temperature for 15 min was sufficient to ensure complete complexation of the aluminium.

Investigation of impurities

Twenty impurities commonly found in plutonium metal were investigated to determine their effect on the aluminium determination. The results are shown in Table II, and indicate that only molybdenum and titanium are apt to cause interference at ratios (to aluminium) of less than 1:1, whereas chromium, lead, and uranium will interfere at ratios greater than 1:1, 5:1, and 3:1, respectively. The remainder of the impurities will not interfere unless the ratio is 10:1 or greater. It is unlikely that any of the impurities would ever be present in concentrations high enough to interfere, except for molybdenum and titanium.

Titanium[13] and molybdenum[14] both form anionic chloride complexes in concentrated hydrochloric acid. Aluminium does not.[15] Titanium and molybdenum could, therefore, be separated from aluminium by passing a solution of these elements

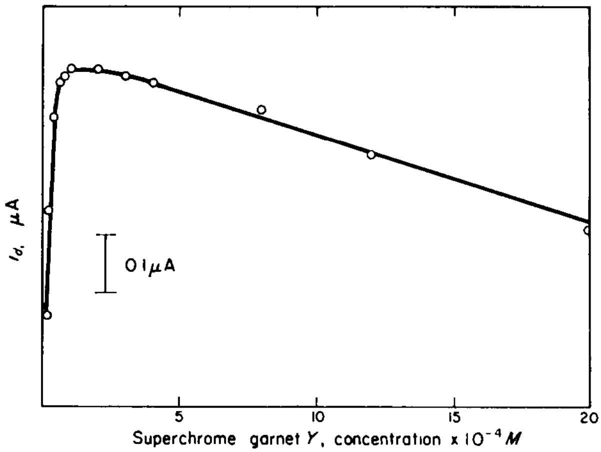

FIG. 2.—Variation of the diffusion current with the concentration of Superchrome Garnet Y
Aluminium, 0·400 μg/ml; acetate buffer 0·2 ml/ml; pH 3·40.

TABLE II.—INVESTIGATION OF IMPURITIES

Ion added	Weight ratio ion/Al	Recovery of Al, %
Ag	100:1	*a*
BO_3^{3-}	100 1	*a*
Ba	100 1	*a*
Ca	100:1	91
	50 1	*a*
Cd	100:1	110
	25·1	*a*
Cr(III)	100:1	193
	1·1	*a*
Cu(II)	100.1	*b*
	10:1	*a*
Fe(III)	100 1	21
	10·1	*a*
Ga(III)	100.1	*a*
K	100 1	*a*
Mg	100·1	*a*
Mn(II)	100 1	*a*
Mo(VI)	100·1	*b*
	0·2.1	*a*
Ni	100 1	86
	50.1	*a*
Pb	100 1	417
	5 1	*a*
SiO_4^{2-}	100 1	*a*
Sr	100·1	*a*
Ti(III)	100 1	515
	0·05.1	*a*
U(VI)	100 1	215
	3:1	*a*
Zn	100·1	*a*

a Error < ±8%.

b No peak at −0·510 V *vs* Hg pool. SGY blocked by added ion forming stronger complex than Al–SGY.

in concentrated hydrochloric acid through an anion-exchange resin. The titanium and the molybdenum would be retained on the resin and the aluminium would pass through.

Analysis of standard aluminium solutions

Eighteen aluminium solutions covering the range 0·020–0·800 μg of aluminium per ml were analysed as described above, except that plutonium was absent. The recovery was 97·0–104·2%, average 99·8%.

Recovery of aluminium in the presence of plutonium

The effect of plutonium on the determination of aluminium was examined by spiking plutonium solutions with standard aluminium solutions. Twelve solutions containing 100–200 mg of plutonium were spiked so that the final aluminium concentration ranged from 0·020 to 1·2 μg/ml. These solutions were taken through the sample preparation procedure and analysed. The recovery ranged from 94·6 to 103·4%, average 99·3%.

Some observations on SGY complexes

During investigation of the effect of impurities on the aluminium peak, we found four metallic ions which produced coloured complexes with SGY: copper (dark orange), iron (dark green), gallium (dark orange), and molybdenum (red-orange). The solutions were buffered with the ammonium acetate buffer at pH 3·4. We did not attempt to investigate the possible use of these complexes for the quantitative determination of these ions, though it is possible that one or more of them may be determined by the use of the SGY complex.

Zusammenfassung—Ein Verfahren zur polarographischen Bestimmung von Aluminium in Plutonium wurde entwickelt. Das Plutonium wird durch Anionenaustausch in einem Nitratmedium abgetrennt und das Aluminium im Eluat mit Superchromgranat Y bestimmt. Der Aluminium Konzentrationsbereich in den polarographierten Losungen ist 0,020–0,800 μg/ml Man findet im Durchschnitt 99,3% des Aluminiums mit der relativen Standardabweichung 7,2%. Bei 20 in Plutoniummetall gefundenen Verunreinigungen storten nur Molybdan und Titan wesentlich; beide konnen durch Ionenaustausch entfernt werden.

Résumé—On a élaboré une technique pour le dosage polarographique de l'aluminium dans le plutonium. Le plutonium est séparé par échange anionique dans un milieu nitrate et l'aluminium est dosé dans l'éluat par emploi de Superchrome Garnet Y. Le domaine de concentration de l'aluminium dans les solutions polarographiées est de 0,020–0,800 μg/ml. La récupération moyenne de l'aluminium est de 99,3%, l'écart type relatif 7,2%. Des 20 impuretés communes trouvées dans le plutonium métallique, seuls le molybdène et le titane causent une gêne importante; tous deux peuvent être éliminés par échange ionique.

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COMPUTER CALCULATION OF EQUILIBRIUM CONSTANTS OF SPECIES PRESENT IN MIXTURES OF METAL IONS AND COMPLEXING AGENTS

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Summary—A general computer program is described for the interpretation of pH titration data for mixtures containing the ions of up to two metals and up to two ligands. The program, which employs the non-linear least-squares method, may be used to calculate equilibrium constants for hydrolysed metal ions, protonated ligands, and simple, protonated, hydrolysed, polynuclear, and mixed complexes.

IN RECENT years many computer programs have been developed for calculating the dissociation constants of acids and bases, and the stability constants of metal complexes, from pH titration data. The more advanced of these programs use one of two mathematical approaches. The first is the non-linear least-squares method, long used by crystallographers in the reduction of X-ray data. The technique has been applied to pH titration data for simple systems by several workers,[1,2] but was expressed in more general computer programs by Rush, Johnson, and Kraus,[3] and by Tobias.[4] The latter's program has since been developed, and its efficiency improved.[5] The modified program, which was called GAUSS, has proved very useful in calculating the equilibrium constants of the various species present in solutions containing one metal and one ligand.[6,7]

The second main approach, due to Sillén and co-workers, is used in programs employing the "LETAGROP" or "pit-mapping" approach.[8–11] With this technique the problem is still to minimize an error-square sum, but now this is defined as a function of the n variables, which may be expressed as a paraboloid in $(n + 1)$ dimensional space, and the calculation is designed to seek the minimum or "pit" in such a surface.

These methods have been used for individual systems containing more than one metal or ligand (where mixed complexes may be formed), and a general method has been described for treating data for these systems, but its use was restricted to systems containing only one unknown constant.[12]

This paper describes a new computer program, SCOGS (*s*tability *c*onstants *o*f *g*eneralized *s*pecies), which employs the conventional non-linear least-squares approach. The program is written in FORTRAN IV. It is capable of calculating simultaneously, or individually, association constants for any of the species formed in systems containing up to two metals and two ligands, provided that the degree of complex formation is pH-dependent. The method can readily be extended to deal with more complicated systems. Thus SCOGS, like GAUSS, may be used to analyse appropriate pH titration data to yield acid association constants (and hence pK_a's), metal-ion hydrolysis constants, stability constants of simple complexes (ML, ML_2,

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etc.) and stability constants of polynuclear species M_2L_3, M_3L_4H, $M_2L_2OH_2$, *etc.*). In addition SCOGS may be used to calculate constants for "mixed" complexes containing two different metals, or two different ligands. In fact, for a mixture of two metals A, B and two ligands S, T, association constants may in principle be calculated with the program for any species *j* which can be described by the general formula

$$A_{A_j}B_{B_j}S_{S_j}T_{T_j}(OH)_{W_j}$$

where A_j, B_j, S_j, T_j are positive integers, or zero, and W_i is a positive integer (for a hydrolysed species), zero, or a negative integer (for a protonated species). The constant calculated is the "practical" overall formation constant β_j given by the expression

$$\beta_j = \frac{[A_{A_j}B_{B_j}S_{S_j}T_{T_j}(OH)_{W_j}]}{[A]^{A_j}[B]^{B_j}[S]^{S_j}[T]^{T_j}\{OH\}^{W_j}}$$

where square brackets [ ] denote concentrations, and braces { } denote activities. Here, and elsewhere in this paper, charges on ionic species are omitted for clarity.

Main program

The program is in three parts, the main program and two subroutines, one of which (SUB760) is a standard IBM matrix inversion routine, and will not be described further.

The main program deals with the input of data, the setting up, and solution of the least-squares equations and the output of results. The general approach of the least-squares calculation has been described elsewhere,[13] but some aspects of its application to the present program will be discussed here.

The calculation of GAUSS consisted of minimizing the sum of the squares of the weighted residuals in "analytical hydrogen ion concentration". The value of this quantity, a measure of the concentration of titratable acid present, varied considerably in the course of a titration, thus it appeared necessary in the calculation to apply a statistical weight equal to the reciprocal of the calculated variance of the residual. However it was observed that when a constant weight was applied negligible change in the calculated constants resulted.

In SCOGS, refinement consists of minimizing the sum of the squares of residuals in titre, $\Sigma_i R_i$, where, for the *i*th point, R_i = (actual titre of base) − (titre calculated from input data using current estimates of the constants, and the experimental value of pH). The variance of R_i is not expected to change as markedly during a series of experiments as it does when R_i is defined in terms of analytical hydrogen ion concentration, and for this reason constant (unit) weights have been used in this program. This simplifying step is further justified by the fact that where SCOGS and the weighted least-squares program GAUSS may be applied to the same experimental data, the two programs yield constants which agree to within their estimated standard deviations.

The calculation begins with the reading of the input data, formats and other details of which are provided, with a listing of the program, in the Appendix. The constitution of each species (*i.e.*, values of A_j, B_j, S_j, T_j and W_j) must be given together with an estimate of the overall formation constant. The present version of the program may be used for systems containing up to twenty complex species. If the value of any constant is accurately known, it may be retained at this value in the calculation, otherwise it may be adjusted by the computer to give the best fit to the data.

In accurate work it is usual to carry out titrations at several reagent concentrations. SCOGS will accept data for any number of experiments for a given system, up to a total of 200 titration readings, and the constants are then adjusted to fit all points simultaneously. For each experiment the initial conditions are read in, followed by the titration results. The computer then combines the data for individual experiments and subsequently the data for all experiments are treated together. Other input data are values for the ionic product of water and activity coefficient of hydrogen ion under the experimental conditions, and finally the computer requires certain information relating to the execution of the calculation, number of cycles of refinement, the constants to be adjusted, *etc.*

After reading the data and carrying out preliminary calculations, the computer begins to calculate for each experimental point the residuals and differential terms required for the solution of the least-squares equations. Initial estimates are first required for each free metal and free ligand concentration. These approximations are then improved iteratively in the subroutine COGSNR until they are satisfactory roots to the four simultaneous equations for total metal and total ligand concentrations. For the first point of an experiment the initial approximations are that free metal concentrations equal the total metal concentrations, and that the free ligand concentrations may be calculated by using the acid association constants of the ligands and assuming no complex formation. Similar initial estimates are used for the nth point when (owing to faulty data) the calculation has failed to converge satisfactorily for the $(n - 1)$th point. Under normal running the final values of the free metal and free ligand concentrations for the $(n - 1)$th point are used as initial estimates for the nth point.

The free metal and free ligand concentrations calculated in this manner are used to calculate the concentrations of all species, and hence the analytical hydrogen ion concentration for each experimental point. This quantity is used in the main program to obtain the calculated titre, and thus the value of the residual R_i.

Progressing through each experimental point, the least-squares equations are built-up, and are solved by matrix inversion to yield the shifts in the constants. The improved constants are then calculated and printed, together with their estimated standard deviations. This cycle is repeated a specified number of times, five usually being sufficient. On completion of the calculation a table is printed showing, for each experimental point, the pH, the experimental titre, the residual, the total concentrations of each metal and ligand, the concentrations of each free metal and free ligand, and finally the concentrations of each complex species. These quantities are all calculated from the final values of the constants. The computer then advances to the next set of experimental data, if more remain, or otherwise moves to the next program.

A number of additional features aid the running of the program. If the increment specified in the input data for use in the numerical differentiation was too small, it is successively increased until the differential term becomes significant. The term is then calculated, and the increment is returned to its input value. In the case of non-convergence in subroutine COGSNR, the residual for the relevant point is set at zero and the calculation is continued. If this occurs more than thirty times in a calculation, that calculation is abandoned and the computer proceeds to the next set of data.

When the shifts in the constants have been calculated, the computer checks their values and reduces any which are excessively large. Also a check is made that the sum of the squares of the residuals is in fact less after adjustment of the constants than at the start of the cycle. If this is not so then the shifts have been too great and the calculated shifts are divided by 2 and applied again.

Subroutine COGSNR

The subroutine COGSNR (*c*oncentrations *o*f *g*eneralized *s*pecies by the *N*ewton-*R*aphson method) is used repeatedly to determine the concentrations of all species in the solution. It employs a generalized form of the Newton—Raphson iteration which has been widely used in the solution of problems involving one or two non-linear equations.[14] The method may however be applied to more complicated problems and its use in solving up to four simultaneous non-linear equations will be discussed here

Let us assume that the total concentrations of the metals A and B, and ligands S and T are A, B, S, and T respectively, and the concentrations of the free (*i.e.* unassociated) components are a, b, s and t respectively. Let these components to be in equilibrium with a series of n complex species, each of which may be described by the general formula above. The concentration of the jth species will then be

$$C_j = \beta_j a^{A_j} b^{B_j} s^{S_j} t^{T_j} \{\mathrm{OH}\}^{W_j}.$$

We may now define a series of functions f_a, f_b, f_s and f_t in terms of the experimental and calculated total concentrations of each component.

$$f_a = A_{\mathrm{expt}} - A_{\mathrm{calc}} = A_{\mathrm{expt}} - (a + \sum_{j=1}^{n} A_j C_j)$$

$$f_b = B_{\mathrm{expt}} - B_{\mathrm{calc}} = B_{\mathrm{expt}} - (b + \sum_{j=1}^{n} B_j C_j)$$

$$f_s = S_{\mathrm{expt}} - S_{\mathrm{calc}} = R_{\mathrm{expt}} - (s + \sum_{j=1}^{n} S_j C_j)$$

$$f_t = T_{\mathrm{expt}} - T_{\mathrm{calc}} = S_{\mathrm{expt}} - (t + \sum_{j=1}^{n} T_j C_j)$$

If a, b, s and t were accurately known, the values of all these functions would be zero. But we can only estimate these quantities, and then we require to calculate the shifts in the values of a, b, s and t (*i.e.*, x_a, x_b, x_s and x_t) which will simultaneously minimize the functions. Expanding by Taylor's series we obtain four simultaneous equations:

$$\begin{aligned} f_a + g_a^a x_a + g_a^b x_b + g_a^s x_s + g_b^t x_t &= 0 \\ f_b + g_b^a x_a + g_b^b x_b + g_b^s x_s + g_b^t x_t &= 0 \\ f_s + g_s^a x_a + g_s^b x_b + g_s^s x_s + g_s^t x_t &= 0 \\ f_t + g_t^a x_a + g_t^b x_b + g_t^s x_s + g_t^t x_t &= 0 \end{aligned}$$

in which $g_a^a = \dfrac{\mathrm{d}}{\mathrm{d}a}(f_a)$, $g_a^b = \dfrac{\mathrm{d}}{\mathrm{d}b}(f_a)$ *etc.* Expressed in matrix notation this becomes:

$$\left|\begin{matrix} g_a^a\, g_a^b\, g_a^s\, g_a^t \\ g_b^a\, g_b^b\, g_b^s\, g_b^t \\ g_s^a\, g_s^b\, g_s^s\, g_s^t \\ g_t^a\, g_t^b\, g_t^s\, g_t^t \end{matrix}\right| \times \left|\begin{matrix} x_a \\ x_b \\ x_s \\ x_t \end{matrix}\right| = \left|\begin{matrix} -f_a \\ -f_b \\ -f_s \\ -f_t \end{matrix}\right|$$

Solution of the equations for x_a, x_b, *etc.* by matrix inversion yields the shifts which are then applied to a, b, *etc.*

In the program described the matrix is built up in four parts, and the calculation is slightly simplified by determining the fractional shifts, *i.e.*, x_a/a, x_b/b, *etc.* The matrix is symmetrical about the diagonal. After application of the shifts the new values of a, b, s and t are used to calculate improved values of f_a, f_b, f_s and f_t, and the process is repeated until the values of these functions are within specified convergence limits. In the present version of the program these limits have been set at 0 00001 % of A, B, S and T respectively. When satisfactory convergence has been achieved the concentration of each species is calculated, as is the analytical hydrogen ion concentration.

The latter quantity (HO in the subroutine) is calculated from an equation of the form

$$\mathrm{HO} = \frac{\{\mathrm{H}^+\} - \{\mathrm{OH}^-\}}{f_\pm} - \sum_{j=1}^{n} w_j C_j$$

where $f_\pm$ denotes the activity coefficient under the experimental conditions. HO, and the various species concentrations, are then returned to the main program.

The subroutine as listed could be used for a system of any number of metals and ligands with changes only in the DIMENSION statement. For systems of up to two metals and two ligands it is very much faster than the subroutine COGS,[15] which could also be used in such a calculation. However, for more complicated systems convergence with COGSNR is unreliable with the IBM 360/50 computer, despite the use of the DOUBLE PRECISION facility. The simpler program COGS is then preferable.

The single subroutine COGSNR may be used unchanged when there are no metals present (*i.e.*, pK_a calculations), or when there are no ligands present (*i.e.*, metal hydrolysis calculations). In such cases, where there is only one ligand or one metal present, there is only one equation to be solved. The present subroutine is clearly less efficient for this purpose than one written to solve a single equation. However the difference in calculation time is minimal, and it has proved convenient to employ the one subroutine for all types of calculation.

CONCLUSIONS

This program has been used successfully in the refinement of data for all of the various types of system for which it was designed. Where both programs are applicable, the results of programs GAUSS and SCOGS are identical, but SCOGS greatly extends the range of systems which may be studied. When the presence of polynuclear complexes is suspected, the new program may be used, as was GAUSS, in the testing of a variety of species, in the search for the set most likely. Where mixed complexes are present these may now be calculated from titration data as easily as may those for simple complexes.[16] Furthermore no approximations need be made for this calculation to be possible. It is not, for instance, necessary to assume that in a mixture of complexes any one species should predominate.

The program may readily be modified to deal with a greater number of metals or ligands, and a version has already been used in calculating constants for a system of one metal with three ligands.[17] Such a system contains many complex species and it is necessary to carry out a large number of titrations, and to analyse the data from each in order to calculate in turn the constants for the various complexes present. However, this may now be done by using the program. There remains, however, one serious limitation to the usefulness of programs of this type. Where reliable constants are to be calculated for many coexistent species, it is essential to have experimental data of the highest attainable accuracy, covering a wide range of experimental concentrations and acidities. Where these conditions are not satisfied the indiscriminate use of these powerful methods may still yield erroneous species or inaccurate constants.

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APPENDIX

Listed below are the data required by the computer to run program SCOGS Each "job" consists of an experiment (*i.e* , titration), or set of experiments, relating to a given system. Constants are adjusted simultaneously to fit as many experiments as are included in the job. The program is designed to treat any number of jobs in turn up to the number specified in the input data. After completion of this number of jobs the computer passes on to the next program.

Input data and formats

1 Number of jobs to be calculated, (I2).
2 Number of experiments in the set of experiments under study, (I2).
3 Number of ligands, number of metals, number of complex species formed (including protonated forms of ligand, hydrolysed metal species, *etc*), (3I2).
4 For each species a card describing its composition, *i.e.*, number of atoms of ligand (1), ligand (2), metal (1), metal (2), number of hydroxyl groups (a positive integer) or of protons (a negative integer), and the logarithm to base 10 of the cumulative association constant, (5I2, F8·4).
5 Number of displaceable protons on ligand (1), and on ligand (2), (2I2).
6 Title of experiment; any characters in columns 1–80, (20A4). This will be printed as heading of output sheet.
7 Initial concentrations of metal (1), metal (2), ligand (1), ligand (2), and inorganic acid (if any present), concentration of titrant base, and total initial volume, (7F10·3). Concentrations are expressed in mole/litre, volumes in ml.
8 A card for each titration-reading bearing values of titre of base, of pH, and of INDEX (a quantity which is zero for all but the last reading of the experiment when INDEX = 1), (2F10 5, 4X, I1)
9 Then return to item 6 to read data for next experiment and repeat until data for all the experiments, as indicated by item 2, have been read.
10 The next card carries the logarithm to base 10 of the ionic product of water, and the activity coefficient of hydrogen ion under the conditions of the experiment (*e g.*, at 20°C, I = 0·1, CKWL = −14·167 and F = 0 78), (2F8·4)
11 The number of cycles desired, five being usually sufficient, followed by the number of constants to be varied, (2I2).
12 A card for each constant to be varied giving the index of the constant (corresponding to the order specified in item 4), and the increment to be applied (as a logarithm) to the constant in the numerical differentiation (*e.g.*, +1·400E-03, which increments the constant by about 0 3%), (I2, E10·3).
13 The computer now returns to item 2 to commence refinement of another set of experiments, unless the total number of jobs, as indicated in item 1, has been treated, when this program ends and the computer advances to the next program.

Variables used in program SCOGS

AC(K)	Initial concentration of inorganic acid for experiment of which point K is a part
ACID	Initial concentration of inorganic acid.
AL(I,J)	Number of atoms of ligand I in species J.
AM(I,J)	Number of atoms of metal I in species J.
AN(J)	Number of hydroxy groups in species J.
B(I)	Association constant for species I in exponential form
BA(K)	Concentration of titrant base used in experiment of which point K is a part.
BASE	Concentration of titrant base.
BB(I,K)	Total concentration of metal I at point K.

BC(I,J)	Elements of least-squares matrix, which is inverted.
C(I)	Concentration of complex species I.
CC(II,JJ)	Elements of least-squares matrix before inversion.
CK(II)	Constant vector.
CKW	Ionic product of water.
CKWL	Ionic product as logarithm to base 10 (*e.g.*, −14·167).
CL(I,K)	Total concentration of ligand I at point K.
CT	Calculated titre.
CT1	Calculated titre with original constant.
CT2	Calculated titre with constant incremented.
CT3	Calculated titre with constant decremented.
CTITR	Calculated titre.
DE(J)	Differential term in setting up normal equations.
DM(I)	Term used in calculating initial estimate of TX(I).
DMY(I)	Term used in calculating initial estimate of TX(I).
DTITR	Value of experimental titre for point in question.
E(J)	Association constant for species J expressed as logarithm to base 10.
ENDP(I)	Number of displaceable protons on ligand I in form in which ligand was added to solution.
EORIG(I)	Reserves value of E(I) at start of each cycle.
F	Activity coefficient of hydrogen ion.
H(I)	Increment to be applied to constant E(J) in differentiation.
HORIG(I)	Reserves value of H(I).
I	Index used among other things to identify a metal or ligand.
ICC	Index used to control numerical differentiation.
ICH(J)	Index = 1 if increment changed for adjustable constant J.
IEOS	Indicator for extreme overshift = 1 if shift greater than 1 log unit.
IFR(NEXP)	Indicator for first reading of experiment number NEXP.
IG(I)	Index for variable constant number.
II	Variable index used in setting up matrix.
INDEX	Index greater than zero for last point of experiment.
INEXP	Index for number of experiments in set.
INCCH	Index = 1 if increment changed
IOS	Indicator for overshift = 1 if shift greater than 0·5 log unit.
IS	Index used to identify constants to be adjusted.
ITN	Index for total number of readings in set of experiments.
J	Index used among other things to identify complex species number.
J1	Integer used in some DO loops.
JJ	Variable index used in setting up matrix.
K	Index used among other things to identify experimental point number.
K1	Integer used in some DO loops.
KK	Index = 1 if last cycle of refinement complete.
KJ	Reserves values of K.
KTN	Counter used in assembling data from several experiments.
L	Index = 0 after printing of standard deviation in titre with initial constants
LTN	Counter used in assembling data from several experiments.
M	Index used in control of numerical differentiation.
ML(I,J)	Number of atoms of ligand I in species J.
MM(I,J)	Number of atoms of metal I in species J.
MN(J)	Number of hydroxyl groups in species J.
MTN	Counter used in assembling data from several experiments.
N	Number of complex species.
NCC	Number of cycles calculated.
NCD	Number of cycles desired.
NCV	Number of constants to be varied
NDP(I)	Number of displaceable protons on ligand I.
NEXP	Number of experiments to be considered simultaneously.
NINCCH(K)	Number of times increment H changed for point K.
NIT	Number of iterations in SUBROUTINE COGSNR.
NJ	Number of jobs to be calculated.
NJD	Number of jobs done.
NL	Number of ligands.

NM	Number of metals
NNCI	Number of non-convergent iterations in COGSNR.
NOR	Number of titration readings in single experiment.
R	Residual.
RO	Value of residual before increment applied.
SQR	Sum of squares of residuals with improved constants.
SQRO	Sum of squares of residuals with initial constants
SQRP	Standard deviation in titre with initial constants.
TITLE	Array which stores title of experiment.
TITR(K)	Experimental titre for point K of experimental set
TITRE(K)	Experimental titre for point K of single experiment.
TL(I)	Total concentration of ligand I in single experiment
TM(I)	Total concentration of metal I in single experiment.
TURM(K)	Sums concentration of acid added as ligands.
TX(I)	Current estimate of concentration of free ligand I.
U(K)	pH at point K of experimental set (as logarithm).
UX	Antilogarithm of pH for a given single point
UXS(K)	Antilogarithm of pH at point K of experimental set
V(K)	Initial volume of experiment of which point K is a part.
VOL	Initial volume for a given experiment.
VOL1	Total volume at a given point of an experiment.
VX(I)	Current estimate of concentration of free metal I
X(I)	Shift to be applied to variable constant I.
X1	Estimated standard deviation in constant.
XAB	Absolute value of X(I)
Y1(I)	Convergence limit for iteration to find total concentration of metal I.
Y3(I)	Convergence limit for iteration to find total concentration of ligand I.
YA	Variance in titre with improved constants.
YB	Standard deviation in titre with new constants.
ZB(I,K)	Total concentration of metal I at point K.
ZL(I,K)	Total concentration of ligand I at point K.
ZU(K)	pH at point K of given experiment.

Variables used only in SUBROUTINE COGSNR

ALO(I)	Total concentration of ligand I.
BO(I)	Total concentration of metal I.
C(K)	Concentration of species K.
HO	Analytical hydrogen ion concentration.
IMNM	Variable used in setting up matrix.
JMNM	Variable used in setting up matrix.
M1	Variable used in setting up matrix.
M2	Variable used in setting up matrix.
SEI(I,J)	Elements of inverted matrix.
SEM(I,J)	Elements of matrix before inversion.
SEV(J)	Elements of constant vector.
SHFT(I)	Fractional shift in concentration.
TERM(K)	Variable used in computing species concentrations.
TERN(K)	Variable used in computing species concentrations.
Y2(I)	Convergence parameter for total concentration of metal I.
Y4(I)	Convergence parameter for total concentration of ligand I. Iteration ceases when Y2(I) < Y1(I) and Y4(I) < Y3(I) for all values of I.

PROGRAM SCOGS

```
C     PROGRAM SCOGS
C
C     THIS PROGRAM IS WRITTEN IN FORTRAN IV(E)
C
      DOUBLE PRECISION CK(20),BC(20,20),CC(20,20),BTOT(2),CLTOT(2),
     1Y1(2),Y2(2),Y3(2),Y4(2),E(20),B(20),EORIG(20),TX(2),VX(2),C(20),
     2DE(20),X(20),TURM(200),CTITR,DTITR,R,RO,CT1,CT2,CT3,HO
C
      DIMENSION TITLE(20),ML(2,20),MM(2,20),MN(20),AL(2,20),AM(2,20),
     1AN(20),NDP(2),ENDP(2),TM(2),TL(2),TITRE(60),ZU(60),ZB(2,60),
     2ZL(2,60),U(200),AC(200),BA(200),V(200),TITR(200),TEMP(20,20),
     3BB(2,200),CL(2,200),IG(20),H(20),HORIG(20),UXS(200),NINCCH(200),
     4ICH(20),DM(2),DMY(2),IFR(10)
C
      COMMON C,Y1,Y2,Y3,Y4,BTOT,CLTOT,TX,VX,HO,B,
     1ML,MM,MN,AL,AM,AN,NL,NM,N,UX,F,CKW,NIT,NNCI,KJ
C
   99 FORMAT (I2)
  101 FORMAT (I2)
  102 FORMAT (20A4)
  103 FORMAT (1X,20A4)
  104 FORMAT (//8X,'L1  L2  M1  M2  OH  LOG.BETA'/)
  105 FORMAT (3I2)
  107 FORMAT (5I2,F8.4)
  108 FORMAT (1X,I3,2X,5(2X,I2),3X,F8.4)
  110 FORMAT (2I2)
  111 FORMAT(/' NDP(',I1,') = ',I2)
  113 FORMAT (7F10.3)
  114 FORMAT ( ' INITIAL CONDITIONS'/' M1=',F10.8,' M2=',F10.8,' L1=',F1
     10.8,' L2=',F10.8,' ACID=',F10.8,' BASE=',F10.8,' TOTAL VOLUME=',F7
     2.3)
  116 FORMAT (2F10.5,4X,I1)
  118 FORMAT(' (',I3,' READINGS)'/)
  122 FORMAT (2F8.4)
  123 FORMAT (/' CKWL=',F7.3,5X,'F=',F5.2/)
  124 FORMAT (/' NUMBER OF PARAMETERS  ',I2/' TOTAL NUMBER OF READINGS
     1 ',I3/)
  126 FORMAT (I2,E10.3)
  173 FORMAT (/' INCREMENT FOR VARIABLE CONSTANT ',I2,' RAISED')
  175 FORMAT (/' INCREMENTS CHANGED FOR ',I3,' POINT(S)')
  182 FORMAT (/' OVERSHIFT, VARIABLE CONSTANT NO. ',I2,' X(I)=',1PE10.3)
  183 FORMAT (/' EXTREME OVERSHIFT, VARIABLE CONSTANT NO. ',I2,' X(I)=',
     11PE10.3)
  196 FORMAT (/' THE STANDARD DEVIATION IN TITRE WITH THE INPUT CONSTANT
     1S IS '.1PE11.4/)
  197 FORMAT (/' THE STANDARD DEVIATION IN TITRE IS ',1PE11.4)
  201 FORMAT (/' X1 NEGATIVE')
  202 FORMAT (1X,I2,F12.4,F8.4,2X,'SHIFT=',F7.4)
  206 FORMAT (/' HALF SHIFTS APPLIED FOR NEXT CYCLE')
  207 FORMAT (/' CYCLES CALCULATED ',I2)
  209 FORMAT (//2X,'K',3X,'PH',5X,'TITRE',5X,'RESID',6X,'TM1',8X,'TM2',8
     1X,'TL1',8X,'TL2',8X,'FM1',8X,'FM2',8X,'FL1',8X,'FL2')
  210 FORMAT (12X,'C1',9X,'C2',9X,'C3',9X,'C4',9X,'C5',9X,'C6',9X,'C7',9
     1X,'C8',9X,'C9',8X,'C10')
  211 FORMAT (8X,'C11',8X,'C12',8X,'C13',8X,'C14',8X,'C15',8X,'C16',8X,'
     1C17',8X,'C18',8X,'C19',8X,'C20'/)
  212 FORMAT (1X,I3/4X,F6.3,2F11.6,8(1X,1PE10.3))
  213 FORMAT (8X,10(1X,1PE10.3))
  214 FORMAT (5X,10(1X,1PE10.3))
  999 FORMAT (1H1)
C
C     READS IN DATA
C
      READ (1,99) NJ
      NJD=0
    1 WRITE (3,999)
  100 READ (1,101) INEXP
      READ (1,105) NL,NM,N
      DO 106 J=1,N
  106 READ (1,107)   (ML(I,J),I=1,2),(MM(I,J),I=1,2),MN(J),E(J)
      DO 109 J=1,N
      AN(J)=MN(J)
      DO 109 I=1,2
      AL(I,J)=ML(I,J)
  109 AM(I,J)=MM(I,J)
      READ (1,110) (NDP(I),I=1,2)
      DO 112 I=1,2
  112 FNDP(I)=NDP(I)
      ITN=0
      DO 231 I=1,10
  231 IFR(I)=0
      DO 121 NEXP=1,INEXP
C
C     READS IN TITRATION DATA FOR INDIVIDUAL EXPERIMENT
C
      READ (1,102) TITLE
      WRITE (3,103) TITLE
      READ (1,113) TM(1),TM(2),TL(1),TL(2),ACID,BASE,VOL
      WRITE (3,114) TM(1),TM(2),TL(1),TL(2),ACID,BASE,VOL
```

```
      K=0
      KK=0
  115 K=K+1
      READ (1,116) TITRE(K),ZU(K),INDEX
      IF (INDEX) 117,115,117
  117 NOR=K
      WRITE (3,118) NOR
      DO 119 K=1,NOR
      VOL1=VOL+TITRE(K)
      DO 119 I=1,2
      ZB(I,K)=TM(I)*VOL/VOL1
  119 ZL(I,K)=TL(I)*VOL/VOL1
      KTN=ITN+1
      IFR(NEXP)=KTN
      LTN=ITN+NOR
C
C     COMBINES DATA FOR INDIVIDUAL EXPERIMENTS
C
      DO 120 K=KTN,LTN
      MTN=K-ITN
      U(K)=ZU(MTN)
      AC(K)=ACID
      BA(K)=BASE
      V(K)=VOL
      TITR(K)=TITRE(MTN)
      DO 120 I=1,2
      BB(I,K)=ZB(I,MTN)
  120 CL(I,K)=ZL(I,MTN)
  121 ITN=ITN+NOR
      DO 1210 K=1,ITN
 1210 TURM(K)=CL(1,K)*ENDP(1)+CL(2,K)*ENDP(2)
      WRITE (3,111) (I,NDP(I),I=I,NL)
      WRITE (3,104)
      DO 301 J=1,N
  301 WRITE (3.108) J.(ML(I,J),I=1,2),(MM(I,J),I=1,2),MN(J),E(J)
      READ (1,122) CKWL,F
      WRITE (3,123) CKWL,F
      WRITE (3,124) N,ITN
      READ (1,110) NCD,NCV
      DO 127 I=1,NCV
      READ (1,126) IG(I),H(I)
  127 HORIG(I)=H(I)
C
C     BEGINS REFINEMENT
C
      NCC=0
      ICC=0
      CKW=10.**CKWL
      DO 129 K=1,ITN
  129 UXS(K)=10.**U(K)
      DO 1290 I=1,2
      TX(I)=0.0
 1290 VX(I)=0.0
  130 NCC=NCC+1
      NNCI=0
      SQR=0.0
      SQRO=0.0
      INCCH=0
      DO 131 K=1,ITN
  131 NINCCH(K)=0
      DO 132 J=1,N
  132 EORIG(J)=E(J)
      DO 133 J=1,20
      ICH(J)=0
      CK(J)=0.0
      DO 133 J1=1,20
  133 CC(J,J1)=0.0
      L=0
  134 K=1
      NEXP=1
  135 DO 136 I=1,2
      BTOT(I)=BB(I,K)
  136 CLTOT(I)=CL(I,K)
      J=0
      M=0
      UX=UXS(K)
      DO 138 I=1,2
      Y1(I)=BTOT(I)*0.0000001
  138 Y3(I)=CLTOT(I)*0.0000001
C
C     DETERMINES INITIAL ESTIMATE FOR FREE METAL AND FREE LIGAND CONCENTRATIONS
C
      IF (ICC-1) 139,140,140
  139 IF (K-IFR(NEXP)) 142,143,142
  142 IF (NIT-99) 140,141,141
  143 NEXP=NEXP+1
  141 DO 144 I=1,NM
  144 VX(I)=BTOT(I)
```

```
      DO 146 I=1,NL
      DMY(I)=1.0
      DO 146 J1=1,N
      IF (ML(I.J1))146,146,147
  147 DO 148 K1=1,NM
      IF (MM(K1,J1)) 146,148,146
  148 CONTINUE
      DM(I)=10.**E(J1)*UX**MN(J1)
      DMY(I)=DMY(I)+DM(I)
  146 CONTINUE
      DO 145 I=1,NL
  145 TX(I)=CLTOT(I)/DMY(I)
  140 DO 149 I=1,N
  149 B(I)=10.**E(I)
      KJ=K
C
C     CALLS SUBROUTINE FOR CALCULATION OF ALL FREE METAL, FREE LIGAND, AND
C     SPECIES CONCENTRATIONS
C
      CALL COGSNR
C
      IF (NNCI-30) 150,215,215
  150 CTITR=V(K)*(TURM(K)+AC(K)-HO)/(BA(K)-TURM(K)+HO)
      CT=CTITR
      DTITR=TITR(K)
      R=CTITR-DTITR
      IF (NIT-100) 220,220,221
  221 R=0.0
  220 IF (KK) 152,152,153
  152 IF (L-1) 154,216,216
  154 M=M+1
      GO TO (155,156,157),M
  155 SQRO=SQRO+R*R
      CT1=CTITR
      RO=R
C
C     BEGINS NUMERICAL DIFFERENTIATION
C
      J=J+1
      IS=IG(J)
  160 E(IS)=EORIG(IS)+H(J)
      ICC=ICC+1
      GO TO 140
  156 CT2=CTITR
      E(IS)=EORIG(IS)-H(J)
      GO TO 140
  157 CT3=CTITR
      E(IS)=EORIG(IS)
      IF (CT2-CT3) 158,159,158
  159 M=1
C
C     INCREASES INCREMENT USED IN NUMERICAL DIFFERENTIATION, IF THIS WAS TOO
C     SMALL
C
      H(J)=H(J)*5.0
      INCCH=1
      ICH(J)=1
      NINCCH(K)=1
      GO TO 160
  158 DE(J)=(CT2-CT3)/(2.*H(J))
      H(J)=HORIG(J)
      IF (J-NCV) 161,162,162
  161 J=J+1
      M=1
      IS=IG(J)
      E(IS)=EORIG(IS)+H(J)
      GO TO 140
C
C     SETS UP MATRIX
C
  162 DO 163 II=1,NCV
      CK(II)=CK(II)-RO*DE(II)
      DO 163 JJ=1,NCV
  163 CC(II,JJ)=CC(II,JJ)+DE(II)*DE(JJ)
  164 K=K+1
      ICC=0
      IF (K-ITN)135,135,167
  167 DO 168 I=1,NCV
      DO 168 J=1,NCV
  168 BC(I,J)=CC(I,J)
      IF (INCCH) 169,169,170
  170 DO 171 I=1,NCV
      IF (ICH(I)) 171,171,172
  172 WRITE (3,173) I
  171 CONTINUE
      NICH=0
```

```
      DO 174 I=1,ITN
      NICH=NICH+NINCCH(I)
  174 NINCCH(I)=0
      WRITE (3,175) NICH
C
C      CALLS MATRIX INVERSION SUBROUTINE, AND SOLVES FOR SHIFTS
C
  169 CALL SUB760(BC,NCV)
C
      DO 176 I=1,NCV
  176 X(I)=0.0
      DO 177 I=1,NCV
      DO 177 J=1,NCV
  177 X(I)=X(I)+BC(I,J)*CK(J)
      IEOS=0
      IOS=0
      DO 178 I=1,NCV
      XAB=DABS(X(I))
C
C     CHECKS SIZE OF SHIFT AND IF GREATER'THAN 1 LOG UNIT REDUCES SHIFT TO
C     0.5. IF ANY SHIFT WAS GREATER THAN 0.5 BUT NONE WERE GREATER THAN 1
C     REDUCES ALL SHIFTS TO HALF VALUE. PRINTS APPROPRIATE MESSAGE
C
      IF (1.-XAB) 179,180,180
  180 IF (0.5-XAB) 181,178,178
  181 IOS=1
      WRITE (3,182) I,X(I)
      GO TO 178
  179 IEOS=1
      WRITE (3,183) I,X(I)
  178 CONTINUE
      IF (IEOS) 184,184,185
  185 DO 186 I=1,NCV
      IF (1.-X(I)) 187,187,188
  188 IF (1.+X(I)) 189,189,186
  187 X(I)=0.5
      GO TO 186
  189 X(I)=-0.5
  186 CONTINUE
      GO TO 190
  184 IF (IOS, 190,190,191
  191 DO 192 I=1,NCV
  192 X(I)=0.5*X(I)
  190 SQRO=SQRO/FLOAT(ITN-NCV)
      DO 193 I=1,NCV
      IS=IG(I)
  193 E(IS)=EORIG(IS)+X(I)
      IF (NCC-1) 194,194,195
  194 SQRP=SQRT(SQRO)
C
C     PRINTS STANDARD DEVIATION IN TITRE WITH INITIAL CONSTANTS
C
      WRITE (3,196) SQRP
  195 L=L+1
      ICC=0
      GO TO 134
  216 SQR=SQR+R*R
      K=K+1
      IF (K-ITN) 135,135,217
  217  YA=SQR/FLOAT(ITN-NCV)
      YB=SQRT(YA)
C
C     PRINTS STANDARD DEVIATION IN TITRE WITH NEW CONSTANTS
C
      WRITE (3,197) YB
      DO 198 I=1,NCV
      IS=IG(I)
      X1=BC(I,I)*YA
      IF (X1) 199,200,200
  199 X1=-X1
      WRITE (3,201)
  200 X1=SQRT(X1)
C
C     PRINTS IMPROVED CONSTANTS, ESTIMATED STANDARD DEVIATIONS, AND SHIFTS
C     FROM FORMER VALUES
C
  198 WRITE (3,202) IS,E(IS),X1,X(I)
      IF (SQRO-YA) 203,204,204
  203 DO 205 I=1,NCV
      IS=IG(I)
      X(I)=0.5*X(I)
  205 E(IS)=E(IS)-X(I)
      WRITE (3,206)
  204 WRITE (3,207) NCC
      IF (NCC-NCD) 130,208,208
C
C     AFTER FINAL CYCLE OF REFINEMENT CALCULATES AND PRINTS TABULATION OF
C     QUANTITIES OF INTEREST USING FINAL VALUES OF CONSTANTS
C
  208 KK=1
```

```
      DO 230 I=1,20
  230 C(I)=0.0
      WRITE (3,209)
      WRITE (3,210)
      WRITE (3,211)
      GO TO 134
  153 WRITE (3,212) K,U(K),TITR(K), R,BB(1,K),BB(2,K),CL(1,K),CL(2,K),
     1VX(1),VX(2),TX(1),TX(2)
      WRITE (3,213) (C(J),J=1,10)
      WRITE (3,214) (C(J),J=11,20)
      K=K+1
      IF (K-ITN) 135,135,215
  215 CONTINUE
  250 NJD=NJD+1
      IF (NJD-NJ) 1,1000,1000
 1000 STOP
      END
```

```
      SUBROUTINE COGSNR
C
      DOUBLE PRECISION TERM(20),TERN(20),C(20),Y1(2),Y2(2),Y3(2),Y4(2),
     1BTOT(2),CLTOT(2),TX(2),VX(2),BO(2),ALO(2),SEM(20,20),SEI(20,20),
     2SEV(20),SHFT(20),B(20),HO
C
      DIMENSION ML(2,20),MM(2,20),MN(20),AL(2,20),AM(2,20),AN(20)
C
      COMMON C,Y1,Y2,Y3,Y4,BTOT,CLTOT,TX,VX,HO,B,
     1ML,MM,MN,AL,AM,AN,NL,NM,N,UX,F,CKW,NIT,NNCI,KJ
C
  998 FORMAT (' ITERATION DID NOT CONVERGE, POINT NUMBER ',I3)
C
C     CALCULATES CONCENTRATION OF EACH SPECIES
C
      NIT=0
      DO 1 K=1,N
    1 TERM(K)=B(K)*UX**MN(K)
    2 DO 3 K=1,N
    3 TERN(K)=TERM(K)
      IF (NM) 42,42,41
   41 DO 4 K=1,N
      DO 4 J=1,NM
    4 TERN(K)=TERN(K)*VX(J)**MM(J,K)
   42 DO 5 K=1,N
      IF (NL) 5,5,50
   50 DO 6 J=1,NL
    6 TERN(K)=TERN(K)*TX(J)**ML(J,K)
    5 C(K)=TERN(K)
  100 NIT=NIT+1
C
C     CALCULATES EACH TOTAL METAL AND TOTAL LIGAND CONCENTRATION
C
      DO 7 I=1,NM
      BO(I)=VX(I)
      DO 8 K=1,N
    8 BO(I)=BO(I)+AM(I,K)*C(K)
    7 Y2(I)=DABS(BO(I)-BTOT(I))
      DO 9 I=1,NL
      ALO(I)=TX(I)
      DO 10 K=1,N
   10 ALO(I)=ALO(I)+AL(I,K)*C(K)
    9 Y4(I)=DABS(ALO(I)-CLTOT(I))
      IF (NIT-100) 11,11,999
C
C     CHECKS DEGREE OF CONVERGENCE
C
   11 DO 12 I=1,NM
      IF (Y1(I)-Y2(I)) 14,12,12
   12 CONTINUE
      DO 13 I=1,NL
      IF (Y3(I)-Y4(I)) 14,13,13
   13 CONTINUE
 2000 HO=1./UX-CKW*UX
      HO=HO/F
      DO 2001 J=1,N
 2001 HO=HO-AN(J)*C(J)
      IPT=IPT+1
      RETURN
C
C     IF CONVERGENCE INSUFFICIENT SETS UP, AND SOLVES, MATRIX FOR IMP-
C     ROVED VALUES OF EACH FREE METAL AND FREE LIGAND CONCENTRATION
C
   14 M1=NM+1
      M2=NM+NL
 1070 DO 1001 I=1,M2
      DO 1001 J=1,M2
 1001 SEM(I,J)=0.0
      DO 1002 I=1,NM
 1002 SEM(I,I)=-VX(I)
```

```
      DO 1003 I=M1,M2
      IMNM=I-NM
 1003 SEM(I,I)=-TX(IMNM)
      DO 1004 I=1,NM
      DO 1004 J=1,NM
      DO 1004 K=1,N
 1004 SEM(I,J)=SEM(I,J)-C(K)*AM(I,K)*AM(J,K)
      DO 1005 I=M1,M2
      DO 1005 J=1,NM
      DO 1005 K=1,N
      IMNM=I-NM
 1005 SEM(I,J)=SEM(I,J)-C(K)*AM(J,K)*AL(IMNM,K)
      DO 1006 I=1,NM
      DO 1006 J=M1,M2
      DO 1006 K=1,N
      JMNM=J-NM
 1006 SEM(I,J)=SEM(I,J)-C(K)*AM(I,K)*AL(JMNM,K)
      DO 1007 I=M1,M2
      DO 1007 J=M1,M2
      DO 1007 K=1,N
      IMNM=I-NM
      JMNM=J-NM
 1007 SEM(I,J)=SEM(I,J)-C(K)*AL(IMNM,K)*AL(JMNM,K)
      DO 1008 I=1,NM
 1008 SEV(I)=-BTOT(I)+BO(I)
      DO 1009 I=M1,M2
      IMNM=I-NM
 1009 SEV(I)=-CLTOT(IMNM)+ALO(IMNM)
      DO 1010 I=1,M2
      DO 1010 J=1,M2
 1010 SEI(I,J)=SEM(I,J)
C
C     CALLS MATRIX INVERSION SUBROUTINE
C
      CALL SUB760(SEI,M2)
C
      DO 1011 I=1,M2
 1011 SHFT(I)=0.0
      DO 1012 I=1,M2
      DO 1012 J=1,M2
 1012 SHFT(I)=SHFT(I)+SEI(I,J)*SEV(J)
      DO 1013 I=1,M2
      IF (SHFT(I)+0.9999) 1014,1013,1013
 1014 SHFT(I)=-0.9999
 1013 CONTINUE
      DO 1015 I=1,NM
 1015 VX(I)=VX(I)+VX(I)*SHFT(I)
      DO 1016 I=M1,M2
      K=I-NM
 1016 TX(K)=TX(K)+TX(K)*SHFT(I)
      GO TO 2
C
C     EXITS IF NO CONVERGENCE AFTER 100 ITERATIONS
C
  999 WRITE (3,998) KJ
      IPT=1
      NNCI=NNCI+1
      RETURN
      END
```

```
      SUBROUTINE SUB760(A760,N760)
C
      DOUBLE PRECISION A760(20,20)
C
    3 DO 764 K760=1,N760
      CM760=A760(K760,K760)
      A760(K760,K760)=1.0
      DO 765 J760=1,N760
  765 A760(K760,J760)=A760(K760,J760)/CM760
      DO 764 I760=1,N760
      IF(I760-K760)762,764,762
  762 CM760=A760(I760,K760)
      A760(I760,K760)=0.0
      DO 763 J760=1,N760
  763 A760(I760,J760)=A760(I760,J760)-CM760*A760(K760,J760)
  764 CONTINUE
      RETURN
      END
```

Zusammenfassung—Ein allgemeines Rechenprogramm zur Interpretation von pH-Titrationsdaten in Gemischen wird beschrieben, die die Ionen von bis zu zwei Metallen und bis zu zwei Liganden enthalten Das Programm verwendet die nichtlineare Methode der kleinsten Quadrate. Es kann zur Berechnung der Gleichgewichtskonstanten hydrolysierter Metallionen und protonierter Liganden dienen sowie fur einfache, protonierte, hydrolysierte, mehrkernige und gemischte Komplexe.

Résumé—On décrit un programme général d'ordinateur pour l'interprétation des données de titrage pH pour des mélanges contenant jusqu'à deux ions métalliques et deux ligands. On peut utiliser le programme qui emploie la méthode des moindres carrés non linéaire pour calculer les constantes d'équilibre pour les ions métalliques hydrolysés les ligands protonés et les complexes simples, protonès, hydrolysés, polynucléaires et mixtes.

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POLAROGRAPHIC INVESTIGATION OF *syn*-PHENYL 2-PYRIDYL KETONE OXIME*

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Summary—The polarographic reduction of *syn*-phenyl 2-pyridyl ketone oxime to α-(2-pyridyl)benzylamine over the pH range 0·78–12·88 is reported. Two waves are observed, both of which are pH-dependent The complex electrode reaction is discussed and a mechanism advanced to describe the reduction of the oxime group over the pH range considered.

THE *syn*-form of the compound phenyl 2-pyridyl ketone oxime (HPPK), has long been known to act as a chelating agent[1,2] and has been used as an analytical reagent for various metal ions.[3–7] A detailed study of the reaction between HPPK and copper(II) in 50% v/v dioxan–water has been reported.[8] The results were interpreted to suggest that a charged 2:1 complex, $[Cu(HPPK)_2]^{2+}$, may be formed which loses protons stepwise from the oxime groups on titration with alkali, ultimately yielding a neutral complex $[Cu(PPK)_2]$.

There are several reasons for undertaking the present investigation; a need for the determination of HPPK under relatively strongly acidic conditions, for use in evaluating metal complex formation constants;[8] a need for a method of identifying the azomethine function, which is a fundamental group in a large number of macrocycle ligands and their precursors;[9] and possible use of HPPK in amperometric titration of metal ions.

EXPERIMENTAL

Apparatus

A Radiometer Polariter PO4 was used. An H-type cell fitted with a medium porosity sintered-glass disc in the cross-arm had a 4% agar solution saturated with potassium chloride as the salt bridge and a saturated calomel electrode as reference. A coarse-porosity sintered-glass gas-dispersion cylinder was built into the lower portion of the sample compartment to facilitate de-aeration with prepurified nitrogen. A second cell consisted of a 150-ml beaker with a bakelite cover drilled to accommodate the D.M.E., salt-bridge, burette tip, and gas-dispersion cylinder; the reference electrode was a silver-silver chloride electrode immersed in saturated sodium chloride as recommended by Meites and Moros.[10]

The cell resistance were determined according to Meites.[11] All polarograms were recorded for solutions maintained at 25·0 ± 0·1°.

The circuit for the controlled potential electrolysis was that described by Meites and Thomas.[12] The d c. source was a Heathkit power supply; current was measured on a universal Avometer and potentials on a Rubicon Model 2730 potentiometer. The electrolysis cell was of the double diaphram design recommended by Meites,[13] equipped with a mercury pool working electrode, a saturated calomel reference electrode and a platinum auxiliary electrode

A Perkin–Elmer Model 21 (sodium chloride optics) was used to record the infrared spectra, and calibrated with thin polystyrene film.

Reagents

The preparation of *syn*-phenyl 2-pyridyl ketone oxime has been previously described [8,14] Aliquots of $1 \times 10^{-3}M$ aqueous stock solution were diluted with aqueous buffers to give solutions for polarography.

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* Abstracted from the Thesis submitted by L. W. Harrison in partial fulfillment of the requirements for the M.Sc degree at Acadia University, October 1966

Buffers, prepared from reagent grade chemicals and adjusted to constant ionic strength 0·1 with sodium perchlorate, were: perchloric acid, formic acid–sodium formate; acetic acid–sodium acetate; dihydrogen phosphate–monohydrogen phosphate; bicarbonate–carbonate; glycine–sodium hydroxide.

α-(2-Pyridyl)benzylamine was prepared electrochemically: HPPK (1·0 g) dissolved in 0·1*M* hydrochloric acid (200 ml) was electrolysed for 4 hr in the double diaphram cell with 0·1*M* hydrochloric acid in the second chamber, at 0·8 V *vs*. S.C.E., then neutralized with 1*M* sodium hydroxide in an extraction flask. An oil separated, and was extracted with three 25-ml portions of diethyl ether. The ether solution was dried over anhydrous sodium sulphate for 12 hr, and filtered, then hydrogen chloride was bubbled through the solution and gave a white precipitate immediately. This product was filtered off, recrystallized from ether, and dried at 110° (m.p. 242–4°; mixed melting point with a sample differently prepared[16] showed no depression). α-(2-Pyridyl)benzylamine was obtained by

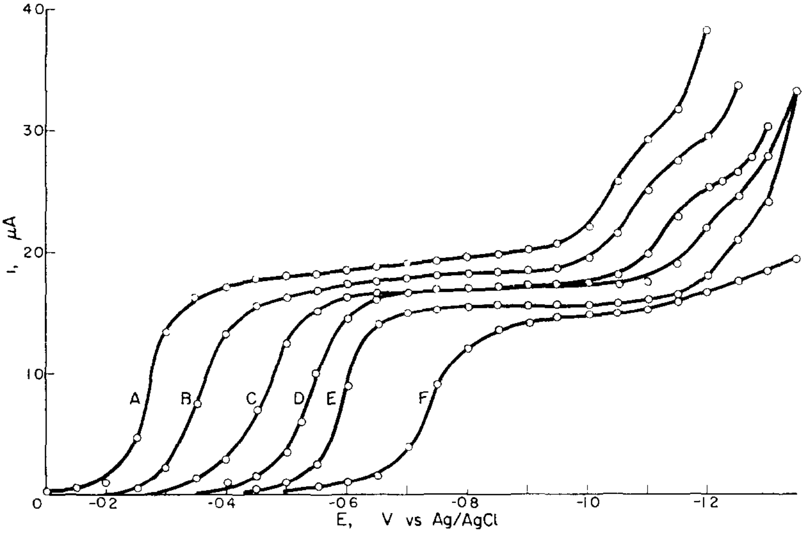


FIG 1.—Polarograms of $10^{-4}M$ *syn*-phenyl-2-pyridyl ketone oxime as a function of pH. $\mu = 0{\cdot}1$, pH *A*—0·78, *B*—1·77; *C*—3·00; *D*—4·00, *E*—5·00, *F*—6·95.
Cell resistance: 280 Ω.

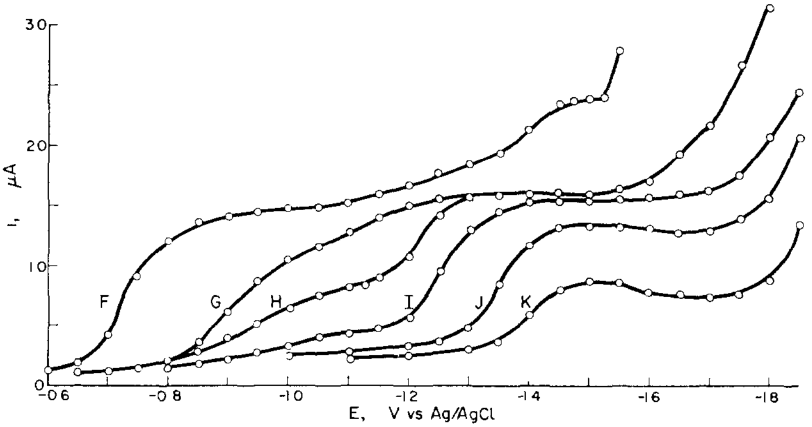


FIG 2.—Polarograms of $10^{-4}M$ *syn*-phenyl-2-pyridyl ketone oxime as a function of pH
$\mu = 0{\cdot}1$; pH· *F*—6·95; *G*—9·00; *H*—9·68; *I*—10·25; *J*—11·89; *K*—12·88;
Cell resistance: 280 Ω.

dissolving the hydrochloride (2 g) in water (25 ml), neutralizing with 1*M* sodium hydroxide, extracting with three 10-ml portions of ether, drying over anhydrous sodium sulphate, filtering, and evaporating the ether. The amine was a colourless oil slowly turning yellow. The amine prepared electrochemically from HPPK and that prepared chemically had identical infrared spectra.

RESULTS AND DISCUSSION

Polarograms were obtained of $1{\cdot}00 \times 10^{-4}M$ HPPK solutions buffered at pH 0·78–12·88 (Figs. 1 and 2).

At pH 0·74 there was a slight change of +3 mV in $E_{1/2}$ an hour after preparation, and a shift of +13 mV after 24 hr, but polarograms for the pH range 2–13 showed no change with time.

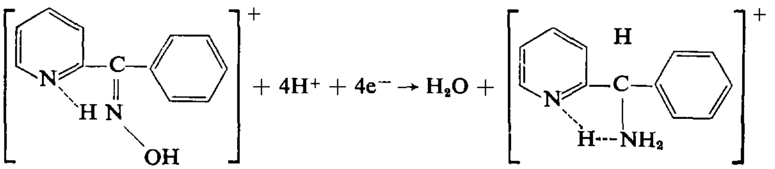
Over the pH range 2–7, solutions of HPPK exhibited a well-defined cathodic wave (A), the $E_{1/2}$ of which became more negative and the height less with increase in pH, the wave disappearing at approximately pH 11 (Table I). At pH 5, the height of wave A varied linearly with $h_{\text{corr}}^{1/2}$ of the mercury column and with concentration of HPPK, indicating that wave A is diffusion-controlled at this pH.

A second wave (B) appeared in polarograms of HPPK at approximately pH 7, increasing in height with increase in pH, to a maximum at about pH 11, and then decreasing rapidly with further increase in pH (Table I).

Although the height of wave A decreased slowly before wave B appeared, when the two waves were present the sum of their currents remained fairly constant ($1{\cdot}5 \pm 0{\cdot}1$ μA).

In the acidic and weakly basic pH range, a poorly defined third wave (C) occurred just before the solution decomposition current appeared. The $E_{1/2}$ of wave C varied with pH and the wave itself was completely obscured at pH values above 10. Wave C was not regarded as typical of the oxime group (*vide infra*) and was attributed to the reduction of the pyridinium grouping. A catalytic hydrogen wave for pyridine, similar in shape to wave C, has been reported by Tompkins and Schmidt[16] and has $E_{1/2}$ more negative than that for wave C (−1·5 V *vs.* S.C.E.). However, picolinic acid has been reported[17] to exhibit a wave with $E_{1/2} = -1{\cdot}17$ V *vs.* S.C.E. at pH 5, and $E_{1/2} = -1{\cdot}5$ V *vs.* S.C.E. at pH 9. The behaviour of this reduction wave of picolinic acid is quite similar to that of wave C. Wave C was not examined further.

At pH values between 0·78 and 3·00 the diffusion current constant I (Table I) is independent of pH. Over this range of pH values, HPPK is present in the bulk of the solution largely as the monoprotonated species, H_2PPK^+. Accordingly, equation (1) may be used to describe the overall reduction of HPPK:



(1)

Support for equation (1) as the description of the over-all reduction of HPPK is derived from the fact that the electrolysis product at pH ~1 is the corresponding protonated amine (*i.e.*, the amine hydrochloride in hydrochloric acid medium). It is recognized that the products of the electrolytic and the polarographic reductions need not be identical, but, in general, the reduction product of an oxime group at the D.M.E. has been shown to be the corresponding amine.[18–22] It is thus concluded that

TABLE I

Wave *A*							Wave *B*						
pH	$E_{\frac{1}{2}}$, V vs S C E.	$-E_{\frac{1}{2}}{}^0$, V vs. S C E	i_{max}, μA	i_{av}, μA	I	αn_a	pH	$-E_{\frac{1}{2}}$, V vs. S C E	$-E_{\frac{1}{2}}{}^0$ V vs S C.E	i_{max} μA	i_{av} μA	I	αn_a
0·78	0·312	0·334	1·86	1·58	7·00	1·10	9·00	1·202	—	0·300	0·310	1·4	—
1·77	0·393	0·415	1·86	1·58	7·03	0·82	9·68	1·258	1·275	0·920	0·715	4·13	0·98
3·00	0·491	0·513	1·76	1·56	6·90	0·80	10·25	1·301	1·320	1·18	1·07	5·31	0·87
4·00	0·577	0·595	1·75	1·54	6·83	1·00	10·91	1·323	1·342	1·25	1·14	5·14	0·86
5·00	0·628	0·641	1·65	1·44	6·40	1·32	11·89	1·392	1·410	1·12	0·925	4·17	0·85
6·95	0·783	0·803	1·48	1·27	5·65	0·86	12·88	1·444	1·459	0·650	0·530	2·40	1·00
9·00	0·942	0·971	1·20	1·03	4·59	0·62							
9·68	0·978	1·005	0·724	0·565	2·52	0·64							
10·25	1·041	—	0·23	0·20	0·89	—							

HPPK undergoes polarographic reduction in acid solution to α-(2-pyridyl)benzylamine.

It is tempting to speculate on a possible mechanism for this reduction. The electrode reaction involving HPPK may perhaps best be described by assuming that it is completely irreversible, *i.e.*, the variations of current with potential do not reflect the change in the position of the relevant equilibria as described by the Nernst equation, or, if a succession of electrode reactions is involved, then one or more of these steps may best be described as totally irreversible. Support for this view comes from the fact that α-(2-pyridyl)benzylamine is not oxidizable under the conditions used in this investigation.

The αn_a values[23] for wave A vary from 0.62 to 1.32 (Table I). A similar variation in αn_a values was reported for α-furildioxime.[21] The large values of αn_a are found in the region of the electrocapillary maximum (−0·6 V *vs.* S.C.E.), the potential region where most organic compounds are likely to be adsorbed onto the mercury surface.[24,25] Accordingly, if the reducible species is positively charged, the apparent value of αn_a will pass through a maximum in the vicinity of the electrocapillary maximum.[24] This is the observed behaviour for wave A of HPPK. This is further support for the interpretation (*vide infra*) that the electroactive species of HPPK giving rise to wave A is positively charged.

Over the pH region 1·7–3, αn_a for wave A is 0·81, which could correspond to $n = 1$ and $\alpha = 0{\cdot}81$ or $n = 2$ and $\alpha = 0{\cdot}4$. The latter value of α would be more consistent with the general case,[23] and since it is generally believed that electrons can be transferred only singly in an electrode reaction, a value of 2 for n would imply that two successive steps cannot be resolved on the time scale implicit in a polarographic measurement.

The value of $dE^0_{1/2}/d(\mathrm{pH})$[23] was found to be −78 mV and from the relationship

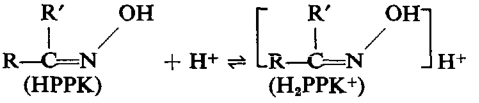
$$\frac{dE_{1/2}}{d\mathrm{pH}} = \frac{-0.03915\,p}{\alpha n_a} \tag{2}$$

a value of $p = 1{\cdot}1$ is obtained if $\alpha n_a = 0{\cdot}81$. Such a value of p suggests that a one-proton transfer step occurs before or during the rate determining electron-transfer step.

Similar values are obtained for wave B: thus $dE^0_{1/2}/d\mathrm{pH} = -56$ mV, and the corresponding value of p is 0 86, again suggesting a one-proton step in the reaction sequence.

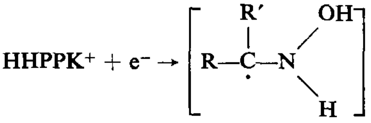
The first step in the postulation of the mechanistic sequence giving rise to either wave A or wave B would be to identify the electroactive species. In this system under the conditions studied, there are three possible species which must be considered as electroactive, or as precursors to the electroactive species. These are H_2PPK^+, HPPK and PPK^-. As a first approximation, PPK^- may be excluded, since the electrode reaction is reductive and the anion exists in the bulk of the solution to a significant extent only at pH >9; this exclusion is in spite of the fact that wave B begins at pH = 9 and as postulated below, the anion is not considered as a precursor in the reduction sequence.

In the following, we propose to argue that both H_2PPK^+ and HPPK are precursors of an electroactive species which we designate as $HHPPK^+$ to indicate that a structural change may take place in H_2PPK^+ (*cf.* Mairanovskii[25]). Table II summarizes the distribution of the species of HPPK as a function of pH, the pH domains of exclusive existence being <2 for H_2PPK^+, 5·5–9·0 for HPPK and >13 for PPK^-. With the work of Laitinen and Wawzonek[26] as model, the following sequence of reactions may be postulated as the mechanism for the reduction of HPPK up to pH = 6·95. For simplicity, the pyridine ring is represented by R, and the phenyl ring by R′.

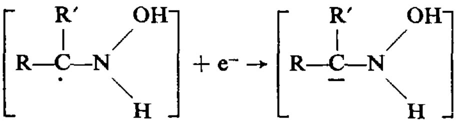


(3a)

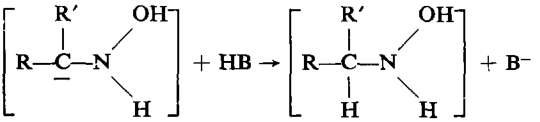
$$H_2PPK^+ \rightarrow HHPPK^+ \qquad (3b)$$



(3c)



(3d)

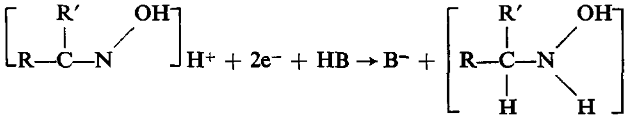


(3e)

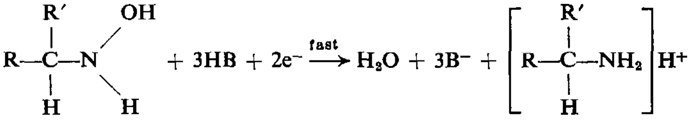
where HB is any proton donor in the solution.

It is suggested that a contributing factor to the rate-controlling step is the position of the equilibrium 3*a*, but that the available data do not permit a categorical statement as to which of steps 3*a*–3*e* controls the rate, if indeed any operates to the exclusion of the others. More definite data may be obtained when techniques for studying rapid electrochemically induced reactions become available. It might be added that it has been assumed[27] in previous investigations carried out in dimethylformamide solution that reactions of type 3*c* are reversible in the thermodynamic sense, but this approach is concerned with the over-all reduction, hence our previously stated assumption of total irreversibility.

Thus, the summation of equations 3*b*–3*e* gives equation (4) which together with equation (5) describes the over-all reaction as represented by equation (1).



(4)



(5)

The formation of the conjugate acid of the amine according to equation (5) may well proceed through the formation of a highly labile imine following loss of the leaving hydroxy group. This postulate requires that the acid HB be involved in two proton-transfer reactions; one to a hydroxide ion, and the other to the amine group of the completely reduced species. Thus, as the buffer is changed with increase in the pH of the solution, the anion B^- becomes more basic; accordingly, the proton transfer reactions implied in equation (5) and specified in equation (3*e*) will become more difficult since it may be presumed that the accepting ability of the base competing with B^- remains invariant throughout the pH range. Thus, wave A must, and does, show a progressive decrease in height with increase in pH.

Support for this mechanistic interpretation for wave A comes from consideration of the values $i = 1{\cdot}48$ μA at pH = 6·95 and $i = 1.86$ μA at pH = 0.78. If we assume that at pH 6·95 an intermolecular transfer of a proton occurs say from some species HB to the azomethine group, then at pH = 0·78 such a transfer could be intramolecular, from the pyridinium nitrogen to the azomethine function (equation 3*b*). The difference in mechanism is reflected in the difference of 0·38 μA in the diffusion current, and when the diffusion current is calculated according to the contributions of the species HPPK and H_2PPK^+, the decrease in wave-height with increase in pH is readily accounted for (Table II). Further support comes from the variation in $E_{1/2}$ with pH for a number of oxime compounds under comparable conditions (Table III)

TABLE II.—THE DIFFUSION CURRENT i_A CALCULATED AS A FUNCTION OF FRACTION* OF TOTAL HPPK PRESENT AS H_2PPK AND HPPK

i_A (experimental), *μA*	i_A (calculated), *μA*	pH	Fraction of HPPK presents as H_2PPK^+	HPPK	PPK^-
1·86	1·86	0·78	1·00	—	—
1·86	1·86	1·77	1·00	—	—
1·80	1·82	3·00	0·89	—	—
1·65	1·63	4·00	0·44	—	—
1·51	1·51	5·00	0·07	—	—
1·48	—	6·95	0	1·00	0
1·20		9·00	—	0·99	0·01
0·724		9·68	—	0·92	0·08
0·23		10·25	—	0·74	0·26
		10·91	—	0·39	0·61
		11·89	—	0·06	0·94
		12·88	—	0·01	0·99

* Calculated from[8] $pK_{a_1} = 3{\cdot}8$, $pK_{a_2} = 10{\cdot}7$

Any substituent which increases the electrophilic character of the azomethine function will result in electroactivity at a more positive potential than that for the unsubstituted oxime.

Over the pH range quoted in Table III, the "ease of reduction" of the oximes may be inferred from the constant in the equation for $E_{1/2}$ (*i.e.*, $E_{1/2}$ at pH 0). The trend parallels the electrophilic character of these compounds as portrayed by the pK_a values. *N*-Methyl-2-pyridinecarbaldehyde oxime is the cation of a quaternary salt, and hence should be excluded from any rigorous comparison with systems which derive their electrophilic character from protonation. It is noteworthy that Gardner and Georgans[19] report values of $E_{1/2}$ at pH = 0 ranging from −0·522 to −0·742 V *vs.* S.C.E. for oximes which do not have a site of positive charge in the system, analogous to wave B for HPPK, which follows the equation $-E_{1/2} = 0{\cdot}061\ \text{pH} + 0{\cdot}667$ over the

Table III —Variation of $E_{1/2}$ with pH for some oximes acid solution

Oxime	pH range	pK_a*	$-E_{1/2}$,
HPPK	0.78–10	3·9†	0.076pH + 0.257
N-Methyl-2-pyridyl-carbaldehyde oxime	0·8–9·9	—	0·043pH + 0·435‡
Pyridine-2-carbaldehyde oxime	0·8–4·6	3·4 ¶(3·8)**	0·037pH + 0·767‡
Dimethylglyoxime	1–3	−0·94††	0·096pH + 0·718‡‡

* Refers to the dissociation of the conjugate acid of the oxime but not necessarily the oxime function

† Reference 8.

‡ Calculated from data in reference 20

¶ C. H. Liu and C. F. Liu, *J. Am. Chem. Soc.*, 1961, **83**, 4169.

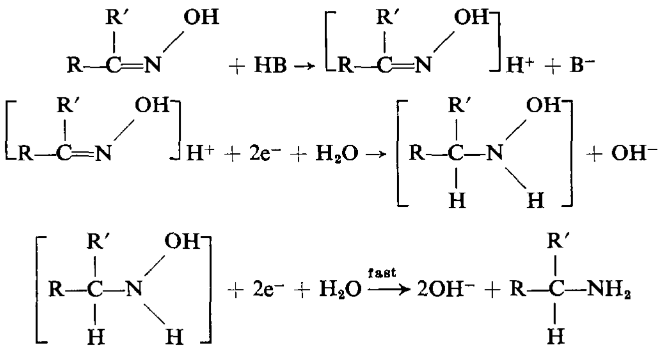
** Reference 20.

†† P R. Ellefsen and L. Gorden, *Talanta*, 1967, **14**, 409.

‡‡ Reference 21

pH range 9–12·8. It thus appears that 2-pyridinecarbaldehyde oxime is anomalous in this respect. The equation for the behaviour of this compound over the pH range 6·4–9·9 was found to be $-E_{1/2} = 0{\cdot}100\,\mathrm{pH} + 0{\cdot}465$ and suggests that the aldehyde oxime is more electrochemically active than the ketone oxime.

It now becomes reasonable to assume that at pH >7·00, HPPK may undergo reduction in a manner analogous to but subtly different from that described by equations (3*a*)–(3*e*). The following sequence of reactions may then describe the mechanism giving rise to wave B.



$$\mathrm{R{-}\overset{R'}{\overset{|}{C}}{=}N{-}OH + HB \rightarrow \left[R{-}\overset{R'}{\overset{|}{C}}{=}N{-}OH\right]H^+ + B^-} \qquad (6a)$$

$$\mathrm{\left[R{-}\overset{R'}{\overset{|}{C}}{=}N{-}OH\right]H^+ + 2e^- + H_2O \rightarrow \left[R{-}\underset{H}{\underset{|}{\overset{R'}{\overset{|}{C}}}}{-}N(OH)(H)\right] + OH^-} \qquad (6b)$$

$$\mathrm{\left[R{-}\underset{H}{\underset{|}{\overset{R'}{\overset{|}{C}}}}{-}N(OH)(H)\right] + 2e^- + H_2O \xrightarrow{fast} 2OH^- + R{-}\underset{H}{\underset{|}{\overset{R'}{\overset{|}{C}}}}{-}NH_2} \qquad (7)$$

It is suggested that (6*a*) and (6*b*) are the rate-controlling steps for this mechanism. This follows the postulate, advanced by Mairanovskii[25] in a polarographic study of semicarbazone-2-acetylthiophene, that the azomethine group required protonation before it became electroactive.

The polarographic method appears to be well suited to the quantitative determination of the free azomethine group in buffered aqueous solution. Extension of the technique to systems containing more than one azomethine group together with a metal ion is under active consideration. For the system containing a 2:1 molar ratio of nickel to HPPK at pH = 1·77, two waves were found. The $E_{1/2}$ values *vs*. S.C E. were −0·5 and −0·9 V. An examination of the nickel(II)–HPPK system will be reported later

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Zusammenfassung: Die polarographische Reduktion von *syn*-Phenyl-2-pyridylketoxim zu α-(2-pyridyl) benzylamin im pH-Bereich 0,78–12,88 wird mitgeteilt. Zwei Stufen werden beobachtet, die beide pH-abhangig sind Die verwickelte Elektrodenreaktion wird diskutiert und zur Beschreibung der Reduktion der Oximgruppe im betrachteten pH-Bereich ein Mechanismus vorgeschlagen.

Résumé—Ond écrit la réduction polarographique de l'oxime de la *syn*-phényl 2-pyridyl cétone en α-(2-pyridyl)benzylamine dans le domaine de pH 0,78–12,88. On observe deux vagues, qui dépendent toutes deux du pH. On discute de la réaction complexe à l'électrode et propose un mécanisme pour décrire la réduction du groupe oxime dans le domaine de pH considéré.

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COMPARISON OF QUANTITATIVE AND SUBSTOICHIOMETRIC DETERMINATION OF CAESIUM FROM FISSION PRODUCTS WITH NITROBENZENE SOLUTION OF LITHIUM DIPICRYLAMINATE

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Summary—A method of determination of ^{137}Cs in a fission product by extraction with a nitrobenzene solution of lithium dipicrylaminate is described. The effect of pH and the amount of reagent on the efficiency of extraction of micro-amounts of caesium has been studied as well as the competing effect of alkali metal salts; the possibility of substoichiometric determination of caesium has been also investigated. Both procedures have been tested with an artificial mixture of fission products.

Various methods for the separation and determination of caesium have been developed which can also be used for the radiochemical determination of nuclear fuel burn-up;[1] a survey has been published by Yamagata.[2] Besides classical and time-consuming gravimetric methods (*e.g.*, the perchlorate,[3] hexacyanocobaltate(III),[4] dipicrylaminate,[5] and other methods), selective sorption methods of ion-exchange on inorganic sorbents such as ammonium phosphomolybdate[6] or various hexacyanoferrates(II)[7,8] suitable for acidic aqueous media or extraction from neutral or alkaline media, have been used. Extraction by a solution of sodium tetraphenylborate (TPB) in amyl acetate (0·05*M* TPB, 0·01*M* EDTA, pH 7) has been used by Leaf in the determination of caesium[9] with a yield of 100·7 ± 0·8%; Davies and Diggle[10] have separated caesium quantitatively by the same method with an error of ±2%. Cesarano *et al.*[11] have isolated caesium from fission products (in the presence of EDTA at pH 6·8) by extraction chromatography on a column of polytrifluorochloroethylene (Kel F) with TPB (in amyl acetate as liquid phase) with a yield of 100·5 ± 0·9% or with dipicrylamine[12] as liquid phase (in nitrobenzene) with a yield of 100·0 ± 0·3% (pH 7, 0·01*M* EDTA). Conditions for caesium and fission product extraction by nitrobenzene solutions of sodium dipicrylaminate (NaDPA) have been investigated in more detail by Kyrš *et al.*[13,14] Alimarin and Perezhogin[15] have pointed out the possibility of using a substoichiometric activation analysis method for caesium by extraction with nitrobenzene solutions of TPB. The substoichiometric method, suggested by Starý and Růžička[16] for activation analysis, has been used mainly for the extraction separation of chelates of the element determined, *e.g.*,[17,18] but a few papers have been devoted to the extraction of co-ordinately non-solvated ion-association compounds.[15,19,20]

The substoichiometric method has not been used for the determination of radionuclides (activity) in fission products. The constancy of chemical yield and further increase of selectivity which result from the substoichiometric method may lead to a simplification and shortening of the procedures and to higher purity of the radionuclide isolated. The aim of this work is to compare quantitative isolation of carrier-free ^{137}Cs with the substoichiometric method, to describe the interfering effect of alkali metal and ammonium ions on the substoichiometric isolation and to compare the purity of radiocaesium isolated from a mixture of fission products by these methods. As a separation method, extraction of caesium by a solution of lithium dipicrylaminate (LiDPA) in nitrobenzene has been used.

EXPERIMENTAL

Chemicals and apparatus

A stock solution of 0·01*M* LiDPA was prepared by dissolution of LiDPA in nitrobenzene purified by distillation.[21] The dilithium salt of ethylenediaminetetra-acetic acid (Li_2Y) used for masking multivalent ions was prepared by neutralization of the acid by a stoichiometric amount of lithium hydroxide.

The concentration of other alkali metal and ammonium ions was adjusted with solutions of the analytical grade nitrates

Buffers used to adjust the pH were prepared from the corresponding acids and lithium hydroxide.

Radioactive isotopes ^{85}Sr, ^{95}Zr–^{95}Nb, ^{106}Ru, ^{137}Cs, and ^{144}Ce were in the form of the nitrates [ruthenium as $RuNO(NO_3)_3$].

The beta-activity was measured with a G.M counter and a decade scaler as usual, the gamma-activity and the purity of ^{137}Cs isolated from the fission product mixture were measured with a 200-channel analyser.

Procedure

In all cases, extraction of caesium was accomplished with equal volumes (4 ml) of the phases. Aqueous solutions containing ^{137}Cs, any other fission products and the required concentration of other components, were neutralized with lithium hydroxide to pH 7 2–8 8 (*o*-Cresol Red indicator); in some cases, the pH was adjusted by adding a buffer. The solutions were shaken in stoppered centrifuge tubes with LiDPA nitrobenzene solution for 30 min to reach extraction equilibrium After centrifugation, aliquot parts of the aqueous and organic phases were evaporated to dryness on aluminium trays and the radioactivity of ^{137}Cs or the fissile radionuclide (in the absence of ^{137}Cs, if required in determination of the fission product extraction) was measured.

RESULTS AND DISCUSSION

Isolation of carrier-free ^{137}Cs

The distribution of carrier-free caesium between the nitrobenzene solution of LiDPA and the aqueous phase was investigated as a function of various conditions in the extraction system.

The dependence of the distribution ratio for the carrier-free caesium, q_{Cs}, on pH is shown in Fig. 1 (curve 1), from which it can be seen that the distribution ratio is (under the given conditions) constant in the pH range 7·5–9·5, which is in agreement with the literature data.[13,14] This pH range was maintained in all other experiments. Curve 2 in Fig. 1 is presented for comparison because it corresponds to the substoichiometric isolation of caesium (substoichiometry $s = 0{\cdot}2$).

At a given pH, the distribution ratio for caesium increases with the concentration of LiDPA as shown in Fig. 2; $q_{Cs} = f(-\log C_{LiDPA})$. The competing effect of lithium ions which appears in the reaction with the reagent leads to a decrease in q_{Cs} (compare curves 2 and 1). This effect of the alkali metal and ammonium ions is shown in Fig. 3, where the dependence $q_{Cs} = f(-\log C_{Me})$ is plotted; the analytical concentration C_{LiDPA} was kept constant The interfering effect of alkali metal ions on the caesium extraction increases in the order Li $<$ Na $<$ NH_4 $<$ K $<$ Rb as found earlier,

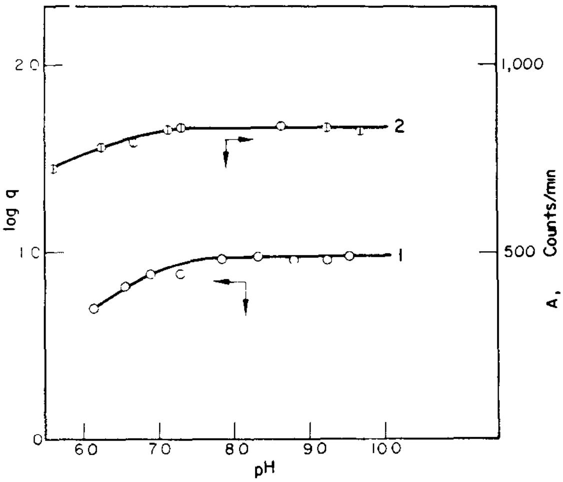

FIG. 1.—Effect of pH on caesium extraction with LiDPA.
1—Isolation of microamounts of ^{137}Cs; $C_{\mathrm{LiDPA}} = 1 \times 10^{-4}M$, $C_{\mathrm{Li}} = 0{\cdot}012M$. *2*—Substoichiometric isolation; $C_{\mathrm{LiDPA}} = 1 \times 10^{-4}M$; $C_{\mathrm{Cs}} = 5 \times 10^{-4}M$; $C_{\mathrm{Li}} = 0{\cdot}012M$, $v = v_0 = 4{\cdot}00$ ml, *A*—activity of the extract sample (cpm); q_{Cs}—distribution ratio for caesium.

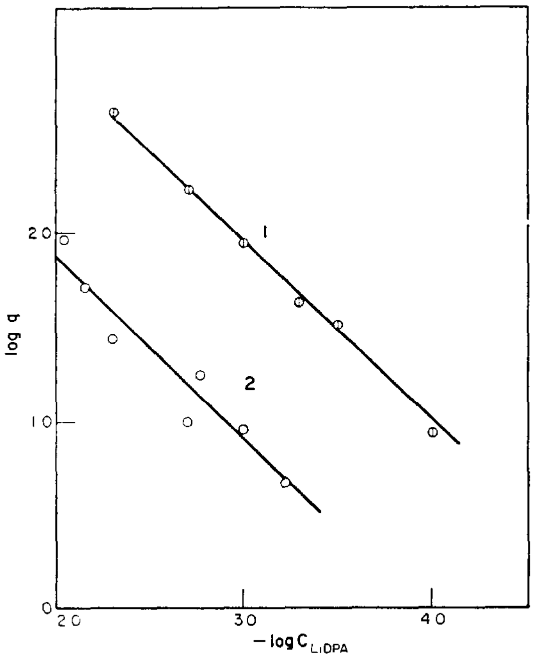

FIG 2.—Dependence of distribution ratio q_{Cs} for ^{137}Cs on LiDPA concentration. *1*—$C_{\mathrm{Li}} = 0{\cdot}012M$, *2*—$C_{\mathrm{Li}} = 1{\cdot}00M$, $v = v_0 = 4{\cdot}00$ ml, pH = 9.

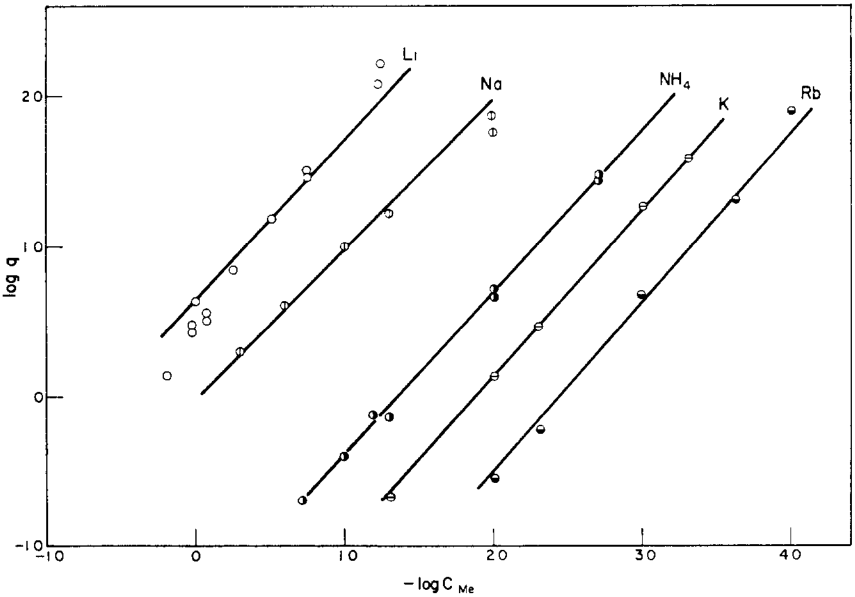

Fig. 3.—Dependence of distribution ratio of carrier-free ^{137}Cs, q_{Cs}, on alkali metal ion concentration, C_{Me}

$C_{LiDPA} = 6 \times 10^{-4}M$, pH = 9, $v = v_0$ = 4·00 ml.

being accompanied with a decrease in the extraction exchange constants of the reaction

$$Cs^+ + MeDPA_{(0)} \rightleftharpoons CsDPA_{(0)} + Me^+ \tag{1}$$

$$K = \frac{[CsDPA]_{(0)}[Me^+]}{[Cs^+][MeDPA]_{(0)}} = q_{Cs}\frac{[Me^+]}{[MeDPA]_{(0)}} \tag{2}$$

where the suffix (0) denotes the organic phase.

With carrier-free concentrations of caesium, $[MeDPA]_{(0)} = C_{LiDPA}$, when $[Me^+] = C_{Me}$, and $C_{Me} \gg [MeDPA]_{(0)}$. The relevant values of the extraction exchange constants $K_{Cs/Me}$, calculated under these conditions, are summarized in Table I; they are in good agreement with the published data.[15,22] The masking of multivalent ions by the disodium salt of ethylenediaminetetra-acetic acid[9,10,13] is, in the separation of caesium from fission products, less convenient than the use of the analogous lithium salt Li_2Y, as follows from the values of the given constants. When

Table I.—Extraction constants $K_{Cs/Me}$ for ^{137}Cs extraction from alkali metal ion solutions with LiDPA in nitrobenzene

Type of reaction	$K_{Cs/Me}$	$K_{Cs/Me}$*	$K_{Cs/Me}$†
Cs/Li	$8·3 \times 10^3$	$1·26 \times 10^4$	1×10^4
Cs/Na	$1·6 \times 10^3$	2×10^3	$2·2 \times 10^3$
Cs/NH_4	83	100	—
Cs/K	23	50	33
Cs/Rb	6·9	5·0	7·2

* Literature data[22]

† The constants for tetraphenylborate [15]

comparing solutions containing the same amount of Li_2Y and Na_2Y, one sees that the q_{Cs} values differ by about an order of magnitude, being higher with the lithium salt. The anion of this masking agent does not affect the q_{Cs} values as could be expected.

Extraction of the carrier-free ^{137}Cs proceeds quantitatively with systems for which pH = 8, $C_{LiNO_3} = 0{\cdot}282M$, $C_{Li_2Y} = 0{\cdot}05M$, and $C_{LiDPA} = 5{\cdot}3 \times 10^{-3}M$. The average value of the extraction yield calculated (by measuring the beta-activity) from 10 parallel runs was 99·97 ± 0·07% caesium.

The reproducibility of the extraction, tested by ^{137}Cs isolation from a model fission product mixture (^{85}Sr, ^{95}Zr–^{95}Nb, ^{106}Ru, ^{144}Ce, and ^{137}Cs) is shown in Table II (A). The radiochemical purity of the ^{137}Cs isolated is evident from the gamma spectra in Fig. 4.

TABLE II.—REPRODUCIBILITY OF DETERMINATION OF RADIOCAESIUM IN MODEL FISSION PRODUCT MIXTURE BY EXTRACTION WITH NITROBENZENE SOLUTION OF LiDPA

	A Carrier-free ^{137}Cs		B Substoichiometric method	
	cpm	*cpm*	*cpm*	*cpm*
1	27708	+319	11593	+292
2	27425	+36	11663	+362
3	26875	−514	11049	−252
4	27429	+40	11149	−152
5	27819	+430	11032	−269
6	27654	+265	11400	+99
7	27396	+7	11321	+20
8	27032	−357	11155	−146
9	27338	−51	11487	+186
10	27221	−168	11162	−139
Average values				
Sample	27389 ± 295		11301 ± 226	
Standard sample	27212 ± 435		11395 ± 200	

Conditions: A—$C_{LiNO_3} = 0{\cdot}282M$, $C_{Li_2Y} = 0{\cdot}05M$; $C_{LiDPA} = 5{\cdot}3 \times 10^{-3}M$.
B—$C_{LiNO_3} = 0{\cdot}282M$; $C_{Li_2Y} = 0{\cdot}05M$, $C_{LiDPA} = 6 \times 10^{-4}M$; $C_{Cs} = 1{\cdot}2 \times 10^{-3}M$.

Substoichiometric separation of caesium

The separation of the caesium carrier (labelled with ^{137}Cs) by a substoichiometric amount of LiDPA from solutions in which the pH is 7·5–10 (Fig. 1, curve 2) was accomplished in the presence of Li_2Y ($C_{Li_2Y} = 0{\cdot}05M$). The curves of the dependence of the extraction yield of caesium (activity in cpm) on the caesium carrier concentration, presented in Fig. 5, have sharp breaks at the point of transition into the substoichiometric region (at the point of equivalence); at higher caesium carrier concentration, the yield of caesium activity does not depend on the carrier concentration. The bend of the curves near the point of equivalence and its shift towards higher values of caesium concentration is caused by a competing reaction of lithium ions with the reagent. The curves represent the course of radiometric titration of the reagent with caesium ions, during which the reaction product was removed by extraction [23]

As in the case of extraction of the carrier-free ^{137}Cs (Fig. 3), the effect of other alkali metal and ammonium ions was studied. The real substoichiometric yield resulting from the competing reactions of these (or other) ions is lower than that for quantitative reaction of the added substoichiometric amount of reagent with caesium, and it can be evaluated from the material balance for the extraction system and from the relationship expressing the extraction exchange constant of the Cs–Me couple [equation (2)].

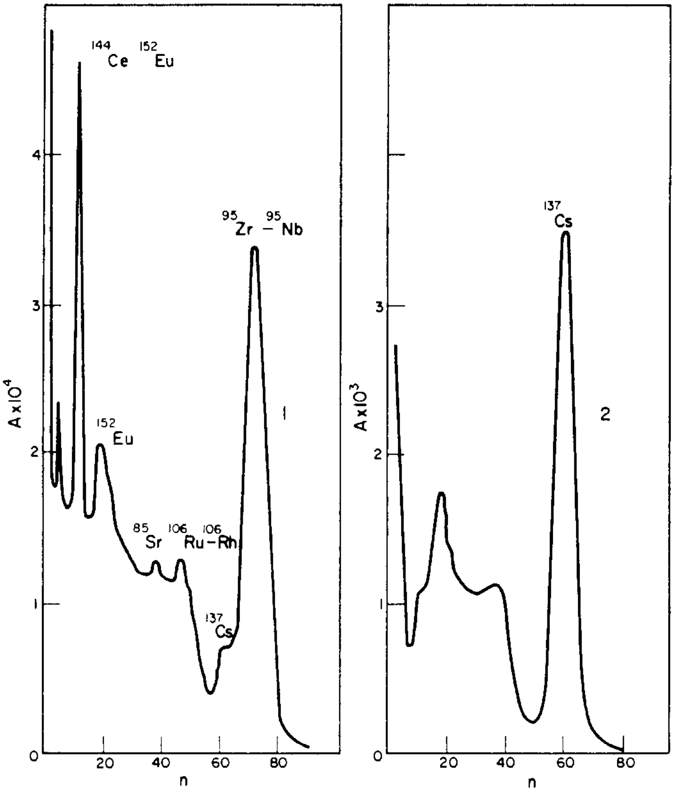

Fig 4 —Gamma-spectrum of model mixture of fission products and isolated ^{137}Cs. *1*—initial mixture; *2*—^{137}Cs isolated; *A*—extract activity (cpm), *n*—number of channel.

The material balance is:

$$C_A \cdot v = [\mathrm{CsA}]_0 \cdot v_0 + [\mathrm{MeA}]_0 \cdot v_0 \tag{3}$$

$$C_{\mathrm{Cs}} \cdot v = [\mathrm{CsA}]_0 \cdot v_0 + [\mathrm{Cs}^+]v \tag{4}$$

$$C_{\mathrm{Me}} \cdot v = [\mathrm{MeA}]_0 \cdot v_0 + [\mathrm{Me}^+] \cdot v \tag{5}$$

$$E = \frac{[\mathrm{CsA}]_0 \cdot v_0}{[\mathrm{Cs}^+] \cdot v} = q_{\mathrm{Cs}} \frac{v_0}{v} \tag{6}$$

where C_A ($= C_{\mathrm{DPA}}$) and C_x are the initial analytical concentrations of the components; the equilibrium concentrations in the aqueous and organic phases are denoted by brackets, E is the effective distribution coefficient, and v and v_0 are the volumes of

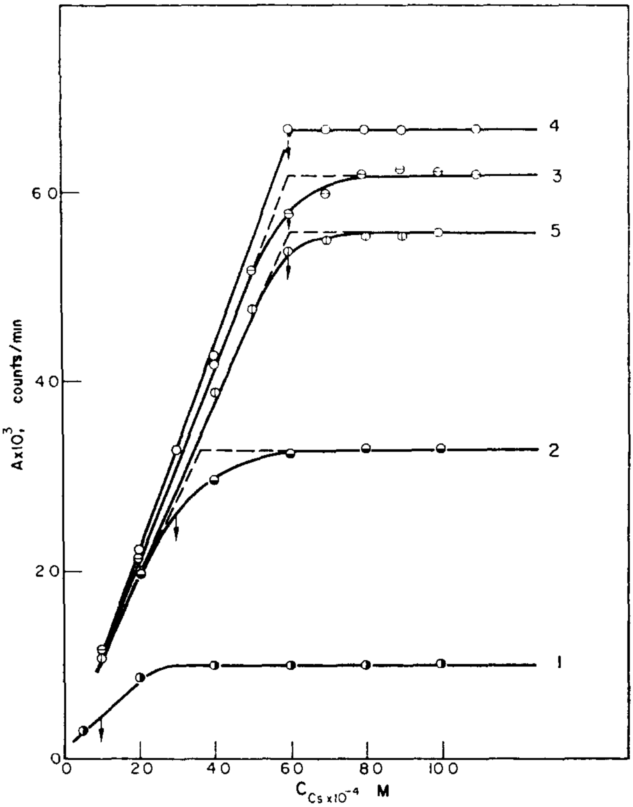

FIG 5.—Dependence of extracted caesium activity, A(ppm) on caesium carrier concentration, C_{Cs}

1—$C_{LiDPA} = 1 \times 10^{-4} M$, *2*—$C_{LiDPA} = 3 \times 10^{-4} M$; *3*—$C_{LiDPA} = 6 \times 10^{-4} M$. *1–3* $C_{Li_2Y} = 0{\cdot}05 M$; $C_{LiNO_3} = 0{\cdot}162 M$; pH ~ 8. *4* $C_{LiNO_3} = 0{\cdot}06 M$, $C_{LiDPA} = 6 \times 10^{-4} M$, pH $= 10$. *5* $C_{LiNO_3} = 0{\cdot}282 M$, $C_{Li_2Y} = 0{\cdot}05 M$; $C_{LiPDA} = 6 \times 10^{-4} M$, pH $= 10$ $v = v_0 = 4{\cdot}00$ ml in all cases.

the aqueous and organic phases, respectively. The equilibrium concentrations expressed in terms of the analytical (total) concentrations and E are:

$$[\mathrm{CsA}]_0 = \frac{E}{E+1} \cdot \frac{v}{v_0} C_{Cs}; \quad [\mathrm{Cs}^+] = \frac{1}{E+1} C_{Cs}$$

$$[\mathrm{MeA}]_0 = \left(C_A - \frac{E}{E+1} C_{Cs}\right)\frac{v}{v_0}; \quad [\mathrm{Me}^+] = C_{Me} - C_A + \frac{E}{E+1} C_{Cs}.$$

On substituting these values into equation (2) for the extraction exchange constant ($K_{Cs/Me} = K$) and rearranging,

$$\frac{C_{Me}}{C_{Cs}} = \left(\frac{C_A}{C_{Cs}} - \frac{E}{E+1}\right)\frac{K+E}{E} \tag{7}$$

which is valid for

$$(C_A/C_{Cs}) > \frac{E}{E+1}.$$

Denoting the substoichiometric ratio by $(C_A/C_{Cs}) = s < 1$, and the portion of reagent isolated in the form of the caesium salt by $(ps)_0$, where $p < 1$,

$$E = \frac{(ps)_0}{1 - (ps)_0} \quad \text{at} \quad v = v_0. \tag{8}$$

On substituting these values into equation (7) and rearranging, the final equations are

$$C_{Me} = \frac{(1-p)}{p}[K(1-ps) + ps]C_{Cs} \tag{9}$$

or

$$p^2 - p\left[\frac{C_{Me}/C_{Cs} + K}{s(K-1)} + 1\right] + \frac{K}{s(K-1)} = 0 \tag{10}$$

[the real value of p corresponds to the negative square root of equation (10)]. From these equations, the yield of caesium at a given carrier concentration as well as the substoichiometry, the concentration of the interfering ion, or the needed carrier concentration, *etc.*, can be calculated. Experimental dependences of the substoichiometric isolation of caesium on the alkali metal concentration were found and the corresponding theoretical curves calculated [from equations (9) and (10)] for the extraction systems in which the relevant concentrations were $C_{Cs} = 8 \times 10^{-4}M$ and $C_{LiDPA} = 6 \times 10^{-4}M$, $s = 0{\cdot}75$. The results presented in Fig. 6, in the form of the dependence $p = f(-\log C_{Me})$ show good agreement of the experimental values with the calculated curves. In Table III are summarized the values of the maximum permissible alkali metal concentrations for 99% isolation of the agent in the form of CsDPA (*i.e.*, with constant substoichiometric yield $100ps = 74{\cdot}25\%$ of caesium carrier at substoichiometry $s = 0{\cdot}75$) together with the values found experimentally. The differences between the values can be explained by a certain inaccuracy in the activity measurement and the constants used in calculation (Table I, column 1).

The accuracy of the radiometric determination of caesium (caesium activity) in the fission product solutions may be affected by co-extraction of other fission products. Therefore, the distribution ratios of some radionuclides were determined under the conditions of complete isolation of the carrier-free ^{137}Cs and the substoichiometric isolation of the caesium carrier The results are shown in Table IV, and compared with the corresponding literature data.[24,25] As can be seen, the distribution ratios, q_{Me}, are 4–6 orders of magnitude lower than the q_{Cs} ratios. The relative decrease in their values for substoichiometric isolation indicates an increase in the selectivity of caesium separation and so, under the given conditions, the co-extraction of other fission products can usually be neglected.

Iron, aluminium and magnesium, the most frequent corrosion products in fission product solutions, do not affect the extraction under the given conditions of substoichiometric isolation of caesium, if their concentration is of the same order as the concentration of the caesium carrier, as can be seen from Table V

The reproducibility of the yield of substoichiometric isolation of caesium from the fission product solution is evident from the values presented in Table II(B). Larger relative deviations (1·0–2·0%) from the average experimental value are due to a poorer

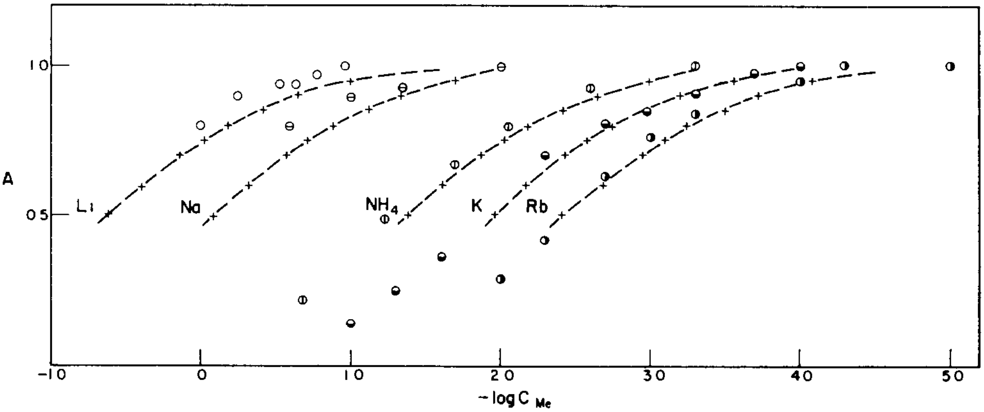

FIG 6.—Dependence of substoichiometric extraction of caesium on competing metal ion concentration

pH $= 9$, $v = v_0 = 4{\cdot}00$ ml, A = relative activity of extract (at $p = 1{\cdot}00$, $C_{LiDPA} = C_{CsDPA} = 0{\cdot}75 C_{Cs}$), the dashed-line curves are theoretical.

TABLE III.—MAXIMUM PERMISSIBLE CONCENTRATION OF ALKALI METAL IONS, C_{Me}, SUBSTOICHIOMETRIC SEPARATION

Alkali element, Me	C_{Me} found, M	C_{Me} calculated, M
Li	$1{\cdot}0 \times 10^{-1}$	$1{\cdot}66 \times 10^{-2}$
Na	4×10^{-2}	$3{\cdot}20 \times 10^{-3}$
NH$_4$	$2{\cdot}5 \times 10^{-3}$	$1{\cdot}82 \times 10^{-4}$
K	$1{\cdot}6 \times 10^{-4}$	$5{\cdot}20 \times 10^{-5}$
Rb	5×10^{-5}	$1{\cdot}98 \times 10^{-5}$

Conditions $s = 0{\cdot}75$ and 99% of agent is extracted in the form of CsDPA

TABLE IV.—EXTRACTION OF SOME FISSION PRODUCTS UNDER CONDITIONS OF SUBSTOICHIOMETRIC AND COMPLETE ISOLATION OF CAESIUM

Fission product	q_{Me} in caesium isolation		
	A substoichiometric	B complete	complete
^{85,90}Sr	$2{\cdot}9 \times 10^{-4}$	$1{\cdot}9 \times 10^{-3}$	$2{\cdot}1 \times 10^{-2}$* $1{\cdot}0 \times 10^{-2}$†
^{95}Zr–^{95}Nb	$1{\cdot}1 \times 10^{-2}$	$2{\cdot}0 \times 10^{-2}$	$3{\cdot}0 \times 10^{-2}$*
^{106}Ru‡	$2{\cdot}9 \times 10^{-4}$		$1{\cdot}2 \times 10^{-3}$* $1{\cdot}0 \times 10^{-1}$†
^{144}Ce	$1{\cdot}4 \times 10^{-3}$	$3{\cdot}2 \times 10^{-3}$	$1{\cdot}0 \times 10^{-2}$*
^{152,154}Eu	7×10^{-4}	$1{\cdot}8 \times 10^{-3}$	
^{170}Tm	$5{\cdot}5 \times 10^{-4}$		

Conditions

A—$C_{LiDPA} = 6 \times 10^{-4} M$, $C_{Cs} = 8 \times 10^{-4} M$, $C_{LiNO_3} = 0{\cdot}162 M$, $C_{Li_2Y} = 0{\cdot}05 M$.
B—$C_{LiDPA} = 5{\cdot}3 \times 10^{-3} M$, $C_{Cs} = 10^{-6} M$; C_{LiNO_3} and C_{Li_2Y} as in A.
* Literature data[25]
† Literature data,[24] distribution ratios for caesium extraction with tetraphenylborate.
‡ Ruthenium as RuNO(NO$_3$)$_3$.

TABLE V.—EFFECT OF Fe, Al, AND Kg ON SUBSTOICHIOMETRIC DETERMINATION OF CAESIUM IN THE PRESENCE OF Li_2Y

Corrosion product, *Me*	C_{Me}, *M*	*cpm*
Fe	$1{\cdot}5 \times 10^{-3}$	3889
	$2{\cdot}5 \times 10^{-3}$	3942
Al	$1{\cdot}5 \times 10^{-3}$	3907
	$2{\cdot}5 \times 10^{-3}$	3857
Mg	$1{\cdot}5 \times 10^{-3}$	3900
	$2{\cdot}5 \times 10^{-3}$	3850
without Me	—	3950

Conditions: $C_{LiNO_3} = 0{\cdot}175M$, $C_{Li_2Y} = 0{\cdot}05M$, $C_{LiDPA} = 6 \times 10^{-4}M$, $C_{Cs} = 8 \times 10^{-4}M$.

accuracy of the determination and of gamma activities (cpm) by graphical integration from the relevant peak for caesium.

CONCLUSIONS

The separation of caesium from solutions at pH 7·5–10 by extraction with nitrobenzene solutions of lithium dipicrylaminate is very reproducible both by complete isolation of carrier-free ^{137}Cs and by isolation of caesium carrier by a substoichiometric amount of reagent. By means of both methods, practically radiochemically pure caesium can be isolated in the presence of Li_2Y ($C_{Li_2Y} = 0{\cdot}05M$) from a mixture of fission products and nuclear fuel solution The selectivity of separation increases when the substoichiometric method is used. Owing to the competing reactions of the reagent with other alkali metal ions, the substoichiometric method can be applied to the determination of caesium only when the concentrations of the alkali elements in the unknown sample and in the comparison solution (with a known activity) are identical. This condition can be easily secured when determining the activity of radiocaesium in nuclear fuel solutions.

On the basis of these facts, the following procedure may be recommended for this purpose. To a solution of fission products or nuclear fuel with a known nitric acid concentration ($C_{HNO_3} = 0{\cdot}2M$), Li_2Y and a caesium carrier are added in such amounts that their concentrations, after dilution to a certain volume, may be $C_{Li_2Y} = 0{\cdot}05M$ and $C_{Cs} = 1{\cdot}2 \times 10^{-3}M$, and the resulting solutions is neutralized with 0·5–1·0*M* lithium hydroxide with *o*-Cresol Red as indicator. Extraction is accomplished by shaking with an equal volume of lithium dipicrylaminate solution in nitrobenzene ($C_{LiDPA} = 6 \times 10^{-4}M$) for 30 min Simultaneously, a standard solution with a known absolute activity of caesium is treated in the same way. The ratio of activities of equal volumes of the sample and the standard solution is then determined.

Zusammenfassung—Eine Methode zur Bestimmung von ^{137}Cs in einem Spaltprodukt durch Extraktion mit einer Lösung von Lithiumdipikrylaminat in Nitrobenzol wird beschrieben Der Einfluß von pH und Reagensmenge auf die Wirksamkeit der Extraktion von Mikromengen Caesium wurde untersucht sowie die Konkurrenz von Alkalimetallsalzen; auch die Möglichkeit einer unterstöchiometrischen Caesiumbestimmung wurde geprüft Beide Verfahren wurden an einer künstlichen Mischung von Spaltprodukten getestet

Résumé—On décrit une méthode de dosage de ^{137}Cs dans un produit de fission par extraction au moyen d'une solution de dipicrylaminate de lithium en nitrobenzène On a étudié l'influence du pH et de la quantité de réactif sur l'efficacité de l'éxtraction de microquantités de céesium, ainsi que l'influence concurrente de sels de métaux alcalins; on a aussi examiné la possibilité de dosage substoechiométrique du caesium. Les deux méthodes ont été essayées avec un mélange artificiel de produits de fission

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RAPID RADIOCHEMICAL SEPARATION OF SELENIUM

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Summary—A rapid separation of selenium based on the extraction of Se(IV) from 4*M* hydrobromic acid into benzene containing 1% of phenol, is described. Recoveries of 99% are achieved in less than 5 min. Oxidizing and reducing agents interfere. The separation is highly selective for selenium.

METHODS in general use for the radiochemical separation of selenium[1] are based mainly on the distillation of selenium tetrabromide or the precipitation of elemental selenium. These methods require multiple stages for the isolation of selenium free from arsenic and germanium, and are time-consuming and unsatisfactory for the study of short-lived selenium isotopes. The object of this investigation was to develop a simple, rapid and selective method for the separation of selenium.

Solvent extraction has the advantage of being simple, rapid and often selective for the separation of an element. Preliminary investigations on the solvent extraction methods available for selenium[2,3] showed that they were not very selective in the presence of arsenic and germanium. In view of the covalent nature of the halides of selenium[4] it was decided to examine the extraction of selenium(IV) from hydrobromic acid into benzene. Preliminary experiments indicated a poor yield for selenium, which was shown to be due to the presence of free bromine in the hydrobromic acid. Selenium (IV) oxidizes bromide to bromine, which in turn can oxidize selenium(IV) to selenium(VI). It was found that addition of phenol[5] to the benzene removed the bromine and increased the extraction of selenium to almost 100%.

Free bromine present in the hydrobromic acid oxidizes the selenium(IV) to selenium(VI) which is not extractable into benzene. The phenol removes the free bromine by forming tribromophenol, and the equilibrium is moved to the right.

$$\mathrm{Se(VI)} + 2\mathrm{Br}^- \rightleftharpoons \mathrm{Se(IV)} + \mathrm{Br}_2$$

When phenol was added to a solution of selenium(IV) in hydrobromic acid, elemental selenium was precipitated. This may be explained by the equilibrium

$$\mathrm{Se(IV)} + 4\mathrm{Br}^- \rightleftharpoons \mathrm{Se(0)} + 2\mathrm{Br}_2$$

being upset by the addition of phenol removing free bromine.

EXPERIMENTAL

Carrier solutions of selenium, arsenic and germanium (0 1 mg/ml) were prepared from the oxides. The germanium dioxide was dissolved in 2*M* sodium hydroxide, and the solution was then made 4*M* in hydrobromic acid The selenium dioxide and arsenic trioxide were dissolved directly in 4*M* hydrobromic acid. The isotopes ^{75}Se, ^{74}As and ^{71}Ge were obtained from the Radiochemical Centre, Amersham, England. All other chemicals were of analytical reagent grade. The liquid scintillator contained 2 g of PPO and 0 2 g of POPOP dissolved in 500 ml of dioxan. An electrothermal mini-stirrer was used and all extractions were carried out in 50-ml Jena centrifuge tubes.

Procedure

The solution containing selenium and other radioisotopes was made 4M in hydrobromic acid and selenium carrier solution was added. This solution was then intimately mixed with an equal volume of benzene containing 1 % w/v phenol, for 1 min The phases were separated by centrifuging, and the aqueous layer was discarded. The organic layer was washed by stirring for 30 sec with 4M hydrobromic acid containing 1 % w/v phenol. The phases were separated and a portion of the benzene layer was withdrawn for counting.

DISCUSSION AND RESULTS

The effect of varying the concentration of phenol was investigated by stirring 5-ml portions of 8M hydrobromic acid containing 0·5 mg of labelled selenium per ml, with equal volumes of benzene containing various amounts of phenol. The results are shown in Fig. 1, from which it can be seen that recoveries are constant for phenol concentrations above 0·5% w/v. In all subsequent experiments, a 1% solution of phenol in benzene was used.

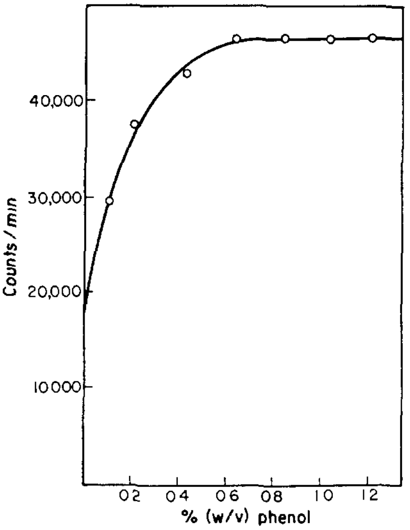

Fig. 1.—Influence of phenol concentration in benzene on the extraction of selenium

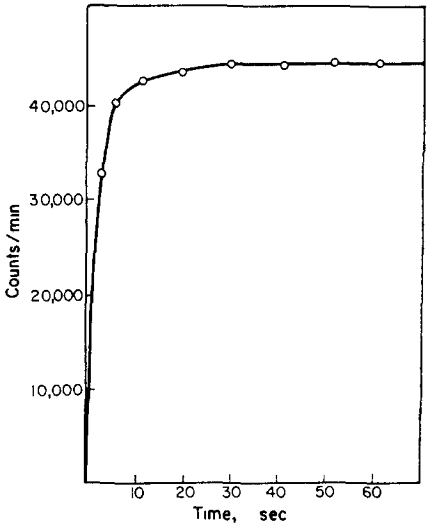

Fig. 2—Time required to reach extraction equilibrium in the extraction of Se(IV) into benzene containing phenol

It is often necessary for the time between the end of the irradiation and the start of counting to be as short as possible. The variation of the quantity of selenium extracted with the time of mixing was investigated, and the results are shown in Fig. 2. Equilibrium is reached after the phases have been intimately mixed for 30 sec. A stirring time of 1 min was chosen for the remaining determinations.

The influence of hydrobromic acid concentration on the extraction of selenium, arsenic and germanium was examined by preparing labelled carrier solutions of the three metals of known acid strength. Portions of these solutions were extracted with equal volumes of benzene containing phenol, for 1 min. From Fig. 3 it is evident that a 4M hydrobromic acid solution is most suitable for the separation of selenium from arsenic and germanium.

The effect of carrier concentration on the reproducibility of the separation was tested in the following manner. A series of 4M hydrobomic acid solutions was prepared, containing accurately known amounts of labelled selenium. Portions of these solutions were extracted with benzene containing phenol as before, and portions of the aqueous and the organic phases were withdrawn for counting. Figure 4 shows the fraction of the selenium extracted as a function of the selenium concentration. The reproducibility of the procedure below a selenium concentration of 0·07 mg/ml was very poor. A selenium carrier concentration of 0·1mg/ml of hydrobromic acid was used for further work.

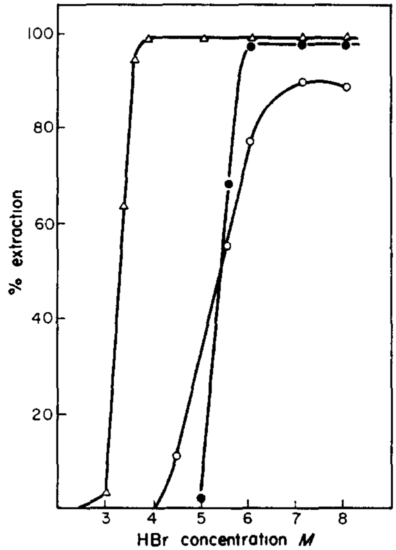

FIG 3 —The extraction of selenium, arsenic and germanium as a function of concentration of hydrobromic acid.

Selenium—△
Arsenic—○
Germanium—●

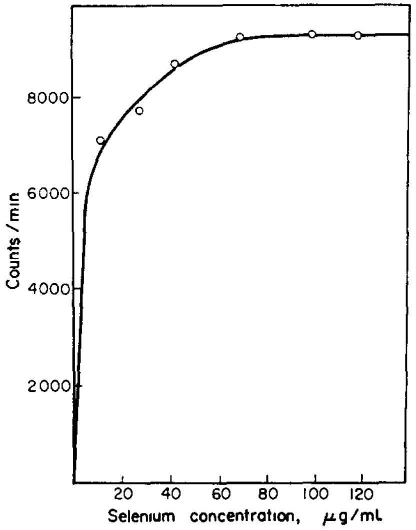

FIG. 4 —Effect of selenium concentration on the extraction of Se(IV) into benzene containing phenol.

Initial selenium activity 9277 cpm.

The effect of various common anions on the extraction of selenium was studied and the results are given in Table I.

Sulphates, chlorides and organic anions such as oxalates and tartrates do not interfere but strong oxidizing and reducing agents seriously affect the yield of selenium. The nitrate ion liberates large amounts of bromine and oxidizes the selenium(IV) to selenium(VI); sulphite ions reduce selenium(IV) to elemental selenium.

TABLE I —EFFECT OF COMMON ANIONS ON SELENIUM RECOVERY

Substance	Concentration, *M*	Recovery of ^{75}Se, %
NaCl	0·1	99·1
NaCl	1·0	98·8
Na_2SO_4	0·1	98·6
Na_2SO_4	0·5	99·0
$NaNO_3$	0·001	97·7
$NaNO_3$	0·01	49·2
$Mg(ClO_4)_2$	0·1	99·7
$(CHOHCOOH)_2$	1·0	98·2
$(COOH)_2$	0·5	99·6
Na_2SO_3	0·1	Se precipitated

The selectivity of the procedure was tested by performing decontamination studies with radioactive tracers representative of most groups of the periodic table. The tracers were added to 4*M* hydrobromic acid solutions containing 0·1 mg of selenium carrier per ml; 5-ml portions of these were extracted with 5 ml of the benzene–phenol solution and the organic layer was washed once with 4*M* hydrobromic acid containing phenol. Table II summarizes the results.

TABLE II.—CONTAMINATION OF SELENIUM EXTRACTED INTO BENZENE FROM 4*M* HYDROBROMIC ACID.

Radioisotope tracer	Activity added to HBr phase, *cpm*	Activity recovered in benzene phase, *cpm*	Contamination, %
^{75}Se	2·15 × 10^5	2·14 × 10^5	99·5 (recovery)
^{74}As	1·28 × 10^6	51	0·004
^{71}Ge	2·56 × 10^5	31	0·01
^{22}Na	1·96 × 10^6	2	0·0001
^{60}Co	1·74 × 10^6	70	0·004
^{106}Ru/Rh	3·34 × 10^5	51	0·02
^{137}Cs	3·16 × 10^6	329	0·01
^{54}Mn	8·16 × 10^4	2	0·002
^{110m}Ag	6·34 × 10^5	4	0·0006
^{125}Sb	3·60 × 10^4	118	0·3
^{204}Tl	5·72 × 10^5	517	0·09
^{131}I	4·68 × 10^5	1404	0·3

There are many instances in which the rapid isolation of selenium in a radiochemically pure form is necessary or desirable. The short-lived isotopes ^{78m}Se $t_{\frac{1}{2}} = 3·9$ min) and ^{83m}Se $t_{\frac{1}{2}} = 69$ sec) can be used for the rapid determination of selenium without the need for expensive equipment if the selenium can be separated in a short time interval.

In this laboratory, investigations into the neutron-deficient isotopes of selenium are being carried out. During the course of this work it was necessary to isolate the 5-min ^{71}Se. This was produced along with a large number of other nuclides when cobalt sulphate was irradiated for 10 min with 140 MeV nitrogen ions in the Manchester Heavy Ion Linac. The nuclear reaction was ^{59}Co (^{14}N, 2n)^{71}Se. The irradiated cobalt sulphate was dissolved in 4*M* hydrobromic acid containing 0·1 mg of selenium carrier per ml. The radioisotopes of selenium were extracted into benzene as described and a 4-ml portion was withdrawn for counting. The decay of the selenium fraction was followed on an automatic gamma-counter. The half-life obtained agrees with that reported for ^{71}Se in the literature.[6]

TABLE III

Operation	Time required, *min*
Transfer of target and dissolution	1·5
Equilibration with benzene	1·0
Separating the phases	0·5
Washing organic layer	0·5
Separating the phases	0·5
Withdrawal and transfer to counter	0·5
Total	4·5

A time-analysis was taken for the separation of the selenium. Table III shows that the selenium was isolated and the counting started within 5 min from stopping the irradiation.

Conclusion

The proposed method for the separation of selenium was shown to be a rapid and efficient method for the radiochemical isolation of radioisotopes of selenium, especially from arsenic and germanium. The procedure is flexible enough to enable it to be adapted to a very fast extraction of selenium. Where the quantitative yield is of secondary importance, more than 90% of the selenium can be extracted into the benzene layer within 10 sec (Fig. 2).

Acknowledgment—We wish to express our appreciation to the staff of the Manchester Heavy Ion Linac for performing the irradiations and to L. S Bark for his helpful discussions.

Zusammenfassung—Es wird eine schnelle Methode zur Abtrennung von Selen beschrieben, die auf der Extraktion von Selen (IV) aus 4*M* Salzsaure in 1% Phenol enthaltendes Benzol beruht. Ausbeuten von 99% werden in weniger als 5 min erzielt Oxidierende und reduzierende Agentien storen. Die Abtrennung ist fur Selen sehr selektiv.

Résumé—On décrit une séparation rapide du sélénium, basée sur l'extraction du Se(IV) à partir d'acide bromhydrique 4*M* en benzène contenant 1% de phénol. Des récupérations de 99% sont atteintes en moins de 5 mn. Les agents oxydants et réducteurs gênent. La séparation est hautement sélective pour le sélénium.

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CATION-EXCHANGE SEPARATION OF METALS IN DIMETHYL SULPHOXIDE-AQUEOUS HYDROCHLORIC ACID MEDIA

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Summary—The behaviour of bismuth, cadmium, copper, lead, silver, tin and zinc on a cation-exchange resin in a solvent system consisting of dimethyl sulphoxide, hydrochloric acid and water was studied The distribution coefficients of these metal ions between liquid and resin were determined as functions of the concentration of dimethyl sulphoxide and of hydrochloric acid. On the basis of the distribution coefficients found, predictions were made as to the possibilities of separating these metals from mixtures. Such separations were confirmed experimentally for bismuth from lead, bismuth from copper, zinc from lead, lead from cadmium, silver from copper, silver from lead, lead from cadmium from zinc, bismuth from lead from zinc, and bismuth from zinc from copper.

THE separation of metals by selective elution from a cation-exchange resin with hydrochloric acid is a well established technique with many applications. The formation of non-dissociated chloro-compounds is probably involved, certainly with the transition metals. The formation of such non-dissociated compounds is favoured in solvents of low dielectric constant and it is not surprising that studies in this field have involved elution with mixtures of water and such organic liquids as methanol, ethanol, isopropanol, acetone, dioxan, and acetic acid.[1-3] The present work is concerned with the separation of metals by selective elution from a cation-exchange resin by hydrochloric acid in mixtures of water and dimethyl sulphoxide, a liquid of high dielectric constant (48·9 at 20°), itself a good solvent for many types of compounds, and an aprotic compound capable of solvating metal ions. In particular, bismuth, cadmium, copper(II), lead, silver, tin(IV), and zinc have been studied, the distribution of each between solvent and resin has been measured at different concentrations of DMSO and of hydrochloric acid, and separations of certain combinations of them have been investigated.

EXPERIMENTAL

Reagents

Metal salts and stock solutions. Perchlorates of zinc, cadmium, copper(II), bismuth, lead, and silver, purchased from the G. Frederick Smith Chemical Company, Columbus, Ohio, were used to prepare 0 05*M* solutions in water. Tin(IV) chloride (Mallinkrodt Chemical Works, St Louis, Missouri) was used to prepare a 0 05*M* solution in 1 0*M* hydrochloric acid All of these solutions were standardized by titration of the metal with EDTA using the procedures described below.

Dimethyl sulphoxide (DMSO), anhydrous(99 9% purity, Matheson, Coleman and Bell, Norwood, Ohio) was used without further purification. Examination of this material by emission spectroscopy revealed only the faintest traces of silver, copper, magnesium and silicon, some 40 other metallic elements being undetectable.

Resin. The strong-acid cation-exchange resin Bio-Rad AG 50W X8 was used. Fine particles of the resin were removed by vigorously back-washing a large column of the resin with water. The resin was conditioned by washing successively with 10% ammonium citrate solution, $3M$ hydrochloric acid, and finally demineralized water until chloride-free. The resin was then slurried with DMSO, then with DMSO plus hydrochloric acid, then with DMSO plus water, and finally with demineralized water. Excess of water was removed by filtration, and the resin was air-dried and then stored in a desiccator over anhydrous magnesium perchlorate. The residue on ignition of 100 g of this resin was 30 mg (300 ppm), spectrographic analysis of the residue showed the presence of aluminium, barium, calcium, copper, gallium, magnesium, manganese, lead, strontium and silicon. These impurities were considered negligible.

Procedures

Standardization and determination. The EDTA solution was standardized against a standard solution of copper nitrate prepared from metallic copper, by titration at pH 5.5 (pyridine buffer) the indicator being Naphthyl Azoxine S[4] (NAS) prepared by dissolving 1 g of the Eastman Kodak Company product in 100 ml of dilute ammonia (1 + 4).

Copper(II) and zinc(II) were determined by direct titration with EDTA in a pyridine buffer (pH about 5.5), NAS being used as indicator. Bismuth(III), cadmium(II), and lead(II) were determined by adding a measured excess of EDTA solution and back-titrating with copper(II) solution, using NAS indicator in a pyridine buffer.

The tin(IV) content of solutions was determined indirectly. To the tin sample was added a measured excess of EDTA, 1.0 ml of concentrated sulphuric acid, and a few glass beads. The solution was boiled for 15 min and then cooled to 50°. The pH was adjusted to 3.5 with sodium hydroxide and hydrochloric acid. A large amount of solid ammonium acetate was added. A measured excess of standard copper solution was then added and the solution back-titrated with standard EDTA solution, with NAS as indicator.

These procedures worked well in the analysis of the aqueous stock solutions of the various perchlorates. However, difficulties were experienced with the end-point in the presence of high concentrations of DMSO. These difficulties were circumvented by diluting the sample with sufficient water to reduce the concentration of DMSO to below 10%.

The stock solution of silver perchlorate was standardized by titration with standard potassium chloride, with dichlorofluorescein as indicator. None of the standard procedures for silver proved satisfactory for the silver in DMSO–hydrochloric acid solution and a procedure was finally devised which involves polarography in a solution deliberately made 80% in DMSO and $1M$ in hydrochloric acid. The cell used, Fig. 1, consisted of three compartments, the left carrying the dropping mercury electrode, the centre a DMSO–lithium chloride salt bridge, and the right a sodium chloride–calomel reference electrode. The electrolyte in all three compartments was replaced after each analysis although the fritted discs were of low porosity and replacement of the centre and right-hand electrolytes may not have been necessary. The electrolyte for analysis was made $1.0M$ in hydrochloric acid, and in the final volume of 100.0 ml contained 80 ml of DMSO and 1.00 ml of Triton X100 solution (0.1% w/v Triton X100 and 0.1% w/v potassium chloride). Oxygen was removed by bubbling oxygen-free nitrogen through the solution. The polarograms were recorded from −0.2 to −0.75 V relative to the calomel electrode. The reduction wave of silver starts at −0.25 V and is continuous with the mercury free wave. It has a maximum which is optimally suppressed by the stated amount of Triton X100. The diffusion current was measured at −0.6 V by drawing a straight line on the polarographic wave between −0.58 and −0.63 V, reading the current at −0.60 V and subtracting the residual current of a blank at the same potential. It was linearly related to the silver concentration up to $2.5 \times 10^{-3}M$, the relative standard deviation being 1% at the $10^{-3}M$ level.

Preparation of solvents. Solvents used for measurement of distribution coefficients were prepared by mixing DMSO and the appropriate hydrochloric acid solution. The composition of the solvents and the hydrochloric acid concentration were calculated from the volumes taken, without regard to changes in volume on mixing. The solvents used for effecting separations on columns were prepared by mixing the DMSO and hydrochloric acid and diluting to volume with water.

Measurement of mass distribution coefficients. Approximately 1 g of dried cation-exchange resin was accurately weighed into a 125-ml conical flask. Then 4.00 ml of the solution of the salt being studied were added and 46.00 ml of liquid consisting of the appropriate volumes and concentrations of DMSO, hydrochloric acid and water. The flask was tightly stoppered and mechanically shaken for 24 hr on a Burrell shaker. The liquid was decanted from the resin and 40.00 ml were taken for the determination of the metal ion remaining in solution. The amount of metal sorbed on the resin was found by the difference between the amount of metal ion added and the amount remaining in solution.

Measurement of sorption rate. Copper was chosen as a representative element for this study. Hydrochloric acid solutions ($0.3M$ in 70% DMSO) were prepared containing exactly 190 μmole of copper(II). The solutions were equilibrated for varying lengths of time and 40.00-ml portions were withdrawn and used for the determination of copper.

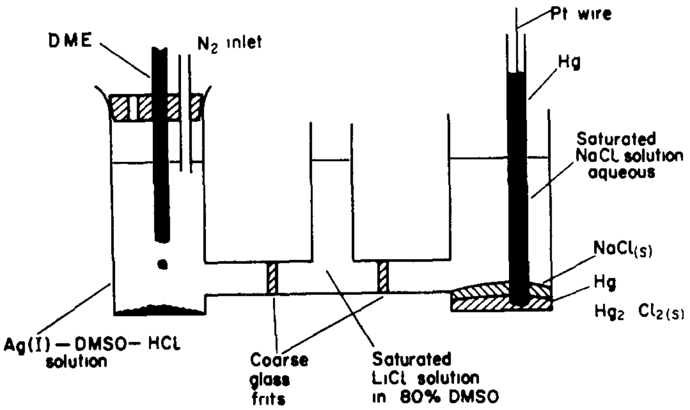

FIG. 1

Separation of mixtures. A slurry of the resin in the first eluting agent was poured into a 1·2-cm bore tube and allowed to settle, sufficient resin being added to give the desired height. A volume of 30 ml of the first eluting agent was then passed through the column to equilibrate the resin and eluting agent.

Portions of 10·00 ml of the 0·05*M* stock solution of the metal being investigated and 1·00 ml of concentrated nitric acid (to prevent hydrolysis) were transferred by pipette into a 50-ml glass beaker and evaporated very slowly on an electric hot-plate to a volume of 1–2 ml or until crystallization began. Then 4·0 ml of the first eluting agent were added and the mixture was swirled to effect the dissolution of any precipitate. Some trouble was experienced at this point, especially with tin and bismuth; if the evaporation was carried too far, the precipitate which formed failed to dissolve, the sample was abandoned, and a new sample was subjected to shorter evaporation.

The solution of the metal in the first eluting agent was transferred to the column and the beaker rinsed with five 1-ml portions of the first eluting agent. After the liquid level had dropped to the top of the resin bed, the reservoir containing the first eluting agent was attached and elution begun. The flow-rate varied from 0·1 ml/min to 0·7 ml/min depending on the column height and on the concentration of DMSO in the eluent. Appropriate volumes of the effluent were collected and analysed for the metal. After the first metal was completely eluted from the column, as evidenced by the analysis of each volume of effluent collected, a second eluting solvent was passed through the column and again portions of the effluent were collected and analysed.

RESULTS AND DISCUSSION

Distribution coefficients

Distribution coefficients were measured by the batch rather than the column method because it is simpler and provides the necessary information more rapidly. The distribution coefficient is defined by

$$D = \frac{\text{mmole metal ion on resin/g of dry resin}}{\text{mmole metal ion in solution/ml of solution}},$$

in which the concentration in the resin is expressed in terms of grams of resin rather than volume of resin; thus, these are properly designated as mass distribution coefficients.

The dependence of the mass distribution coefficients of bismuth(III), cadmium(II), copper(II), lead(II), tin(IV), and zinc(II) on the concentrations of DMSO and of hydrochloric acid are shown in Figs. 2–7, respectively. The effect of increasing concentrations of DMSO and hydrochloric acid in depressing the distribution coefficient are indeed dramatic, extending through three orders of magnitude. The effect is clearly that of promoting the formation of non-dissociated chloro-compounds and DMSO compounds by mass action and decrease in dielectric constant.

The increase in the solubility of the chlorides of bismuth(III), lead and silver with increase in DMSO concentration is striking. Of the seven metals studied, silver presented the greatest problem, owing to the insolubility of the chloride. Stable solutions of silver chloride which remained clear on standing were obtained at high concentrations of DMSO if attention was paid to the order of addition of reagents, which should be DMSO, silver perchlorate stock solution, water, hydrochloric acid. The distribution coefficient for silver, however, was zero for all of the stable solutions of silver chloride, that is for 60–90% DMSO–1*M* hydrochloric acid, 70–90% DMSO–0·5–0·3*M* hydrochloric acid, 80–90% DMSO–0·2–0·1*M* hydrochloric acid.

Equilibrium was rapidly achieved in these systems, the study with copper indicating that 15 min was sufficient, Table I.

Because it was convenient and because the results for copper may not be valid for the other metals studied, the various solutions were shaken for 24 hr. The precision in the measurements is also indicated by the results given in Table I.

Figs. 2–7. Effect of concentrations of DMSO and of hydrochloric acid on the distribution coefficients of various metals between Bio-Rad AG 50W X8 and mixtures of DMSO, hydrochloric acid and water. For silver see text.

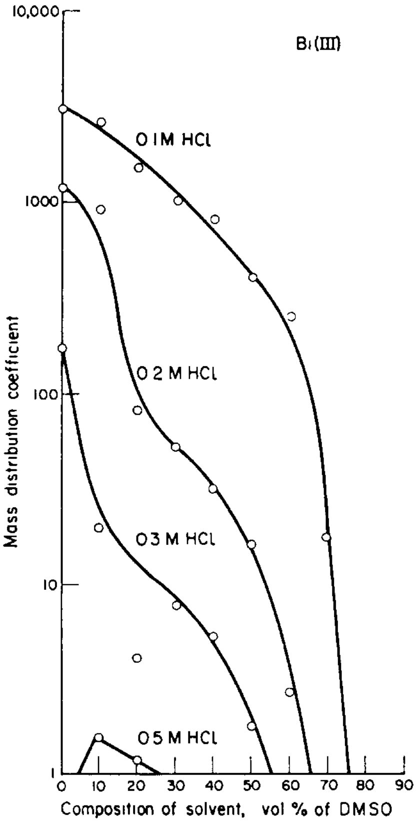

Fig. 2

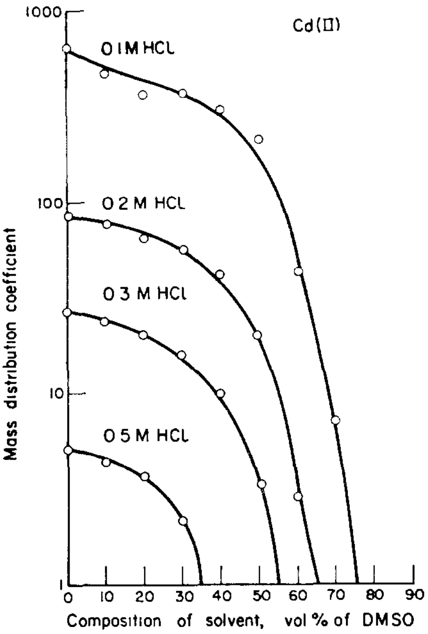

FIG. 3

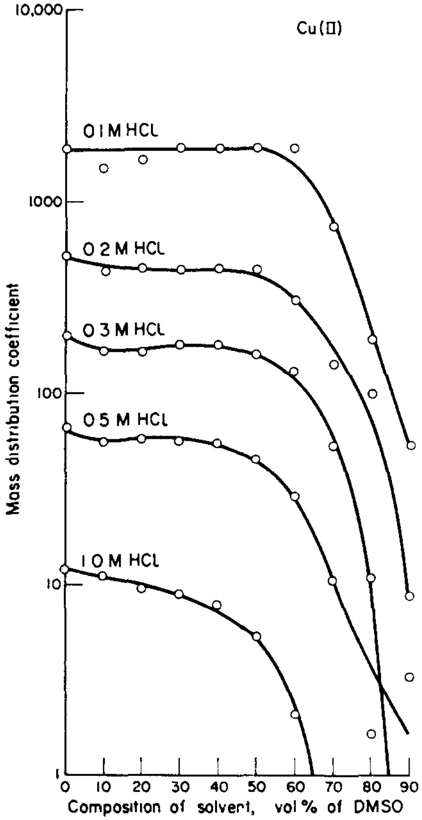

FIG. 4

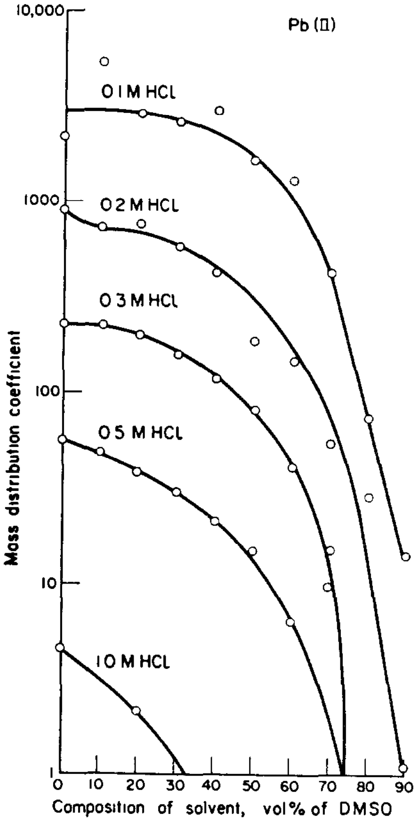

FIG. 5

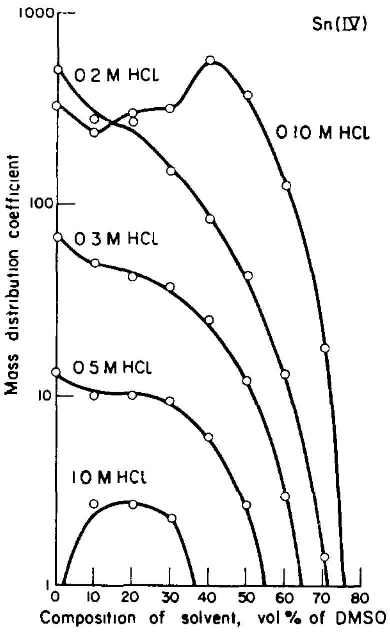

FIG. 6

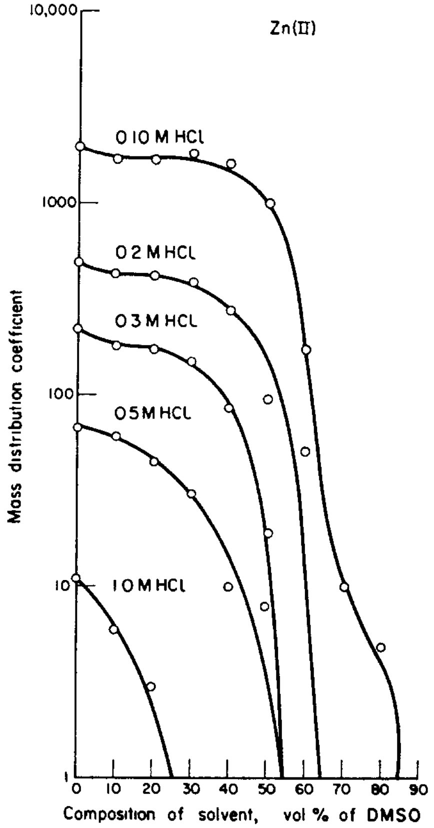

FIG. 7

TABLE I.—RATE AT WHICH EQUILIBRIUM IS ATTAINED IN THE DISTRIBUTION OF COPPER(II) BETWEEN 70% DMSO–0·3M HYDROCHLORIC ACID AND BIO-RAD AG 50W X8 CATION-EXCHANGE RESIN; REPRODUCIBILITY OF MEASUREMENT OF DISTRIBUTION COEFFICIENT

Equilibration time, *hr*	Distribution coefficient
0·25	47·4
0·50	44·7
0·75	46·4
1·0	45·3
2·0	45·5
3·0	44·3
4·0	42·8
5·0	45·9
6·0	44·1
8·0	44·2
10·0	45·5
Average	45·1
Standard deviation	1·3

Separations on columns

Separation of one metal from another was assumed to be feasible if the ratio of the distribution coefficients was greater than 4 (reasonable for a resin bed 1 cm in diameter and 10–20 ml in volume) and if the distribution coefficient of the second metal to pass off the column was greater than 10 (to ensure retention of the second metal while the first passed through). That is, for the metals A and B, D_B/D_A should be >4, and $D_B > 10$. Thus for the mixture of bismuth and lead, the distribution coefficients in 80% DMSO–0·1*M* hydrochloric acid are 0 (the ideal case) and 74, respectively, and in this solvent bismuth should pass through and lead be retained; in 90% DMSO–0·5*M* hydrochloric acid the distribution coefficient of lead is 0 and the lead should be eluted. In practice, this separation worked just as expected, Table II. The separations were successful for the following pairs: bismuth from lead; bismuth from copper(II); zinc from bismuth; zinc from copper(II); zinc from lead; lead from cadmium; silver from copper(II); silver from lead. Separations were also successful for the mixtures of three metals: lead, cadmium, and zinc; bismuth, lead and zinc; bismuth, zinc and copper.

TABLE II.—SEPARATION AND ANALYSIS OF SYNTHETIC MIXTURES OF VARIOUS METALS

	Metal	D_A	D_B	D_C	Eluent			Taken,	Found,‡	Recovery,
					DMSO, %	[HCl],*M*	Volume, *ml*	*mmole*	*mmole*	%
A	Bi*	0	74	—	80	0·1	130	0·442	0·441	99·8
B	Pb*	—	0	—	90	0·5	70	0·564	0·564	100·1
A	Bi*	0	102	—	80	0·2	55	0·442	0·441	99·8
B	Cu(II)*	—	0	—	90	1·0	130	0·694	0·693	99·9
A	Bi*	0	30	—	50	1·0	50	0·475	0·474	99·8
B	Zn*	—	0	—	30	0·5	40	0·442	0·441	99·8
A	Zn*	0	102	—	80	0·2	45	0·474	0·472	99·6
B	Cu(II)*	—	0	—	90	1·0	105	0·694	0·691	99·6
A	Zn†	0	29	—	80	0·2	55	0·475	0·478	100·5
B	Pb†	—	0	—	90	0·3	130	0·564	0·564	100·0
A	Cd†	0	74	—	90	0·3	100	0·564	0·563	99·8
B	Pb†	—	0	—	80	0·1	130	0·575	0·574	99·8
A	Ag†	0	189	—	80	0·1	150	0·498	0·496	99·7
B	Cu(II)†	—	0	—	90	1·0	130	0·695	0·694	99·9
A	Ag†	0	74	—	80	0·1	150	0·498	0·502	100·8
B	Pb†	—	0	—	90	0·3	120	0·564	0·563	99·8
A	Cd†	3	50	105	60	0·2	155	0·574	0·571	99·5
B	Zn†	—	0	29	80	0·2	50	0·474	0·473	99·8
C	Pb†	—	—	0	90	0·3	130	0·564	0·562	99·7
A	Bi†	0	30	30	30	0·5	95	0·442	0·441	99·7
B	Zn†	—	0	29	80	0·2	65	0·474	0·472	99·6
C	Pb†	—	—	0	90	0·3	140	0·564	0·563	99·9
A	Bi†	0	30	57	30	0·5	95	0·442	0·440	99·6
B	Zn†	—	0	102	80	0·2	60	0·474	0·469	99·0
C	Cu(II)†	—	—	0	90	1·0	130	0·694	0·695	100·1

* Column 1·2 × 12 cm

† Column 1·2 × 16 cm.

‡ Average of at least 2 replicates.

Because of the high concentration of DMSO required to hold silver in solution, the number of separations involving silver was quite limited. The separations of silver from copper and from lead were successful; the separation of silver from copper plus lead was also successful but the complete analysis of this three-component mixture was not.

Separations were attempted for several pairs for which the distribution coefficients indicated that the separation should be possible although marginal. Thus, in the separation of bismuth from tin ($D_{\mathrm{Sn}} = 13$, $D_{\mathrm{Bi}} = 2{\cdot}7$ in 60% DMSO–0·2M hydrochloric acid), the tin began to pass off the column before the bismuth was completely eluted. Similarly unsuccessful were the separations of bismuth from cadmium ($D_{\mathrm{Cd}} = 20$, $D_{\mathrm{Bi}} = 4{\cdot}0$ in 20% DMSO–0.3M hydrochloric acid); of cadmium from bismuth ($D_{\mathrm{Bi}} = 18$, $D_{\mathrm{Cd}} = 7{\cdot}3$ in 90% DMSO–0·2M hydrochloric acid); of lead from copper(II) ($D_{\mathrm{Cu(II)}} = 12$, $D_{\mathrm{Pb}} = 0$ in 80% DMSO–0·3M hydrochloric acid); and of lead from tin(IV) ($D_{\mathrm{Pb}} = 15$, $D_{\mathrm{Sn(IV)}} = 0$ in 90% DMSO–0·1M hydrochloric acid).

Zusammenfassung—Das Verhalten von Wismut, Cadmium, Kupfer, Blei, Silber, Zinn und Zink an einem Kationenaustauschharz in einem Losungsmittelsystem aus Dimethylsulfoxid, Salzsaure und Wasser wurde untersucht. Die Verteilungskoeffizienten der genannten Metallionen zwischen Losung und Harz wurden in Abhangigkeit von der Konzentration an Dimethylsulfoxid und Salzsaure untersucht. Auf Grund der gefundenen Verteilungskoeffzienten werden Voraussagen uber die Moglichkeit von Abtrennungen dieser Metalle aus Gemischen gemacht. Experimentell verifiziert wurde die Trennung von Wismut und Blei, Wismut und Kupfer, Zink und Blei, Blei und Cadmium, Silber und Kupfer, Silber und Blei, Cadmium und Zink, Wismut, Blei und Zink sowie Wismut, Zink und Kupfer.

Résumé—On a étudié le comportement des bismuth, cadmium, cuivre, plomb, argent, étain et zinc sur une résine échangeuse de cations dans un système solvant consistant en diméthylsulfoxyde, acide chlorhydrique et eau On a déterminé les coefficients de partage de ces ions métalliques entre le liquide et la résine en fonction des concentrations du diméthylsulfoxyde et de l'acide chlorhydrique. Sur la base des coefficients de partage trouvés, on a fait des prévisions sur les possibilités de séparation de ces métaux de mélanges. De telles séparations ont été confirmées expérimentalement pour le bismuth du plomb, le bismuth du cuivre, le zinc du plomb, le plomb du cadmium, l'argent du cuivre, l'argent du plomb, le plomb du cadmium et du zinc, le bismuth du plomb et du zinc et le bismuth du zinc et du cuivre.

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USE OF A LARGE QUARTZ SPECTROGRAPH FOR THE DETERMINATION OF THORIUM, YTTRIUM AND THE RARE EARTHS IN SILICATES

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Summary—Studies were carried out on the optimum conditions for the successful use of a large quartz spectrograph for the determination of thorium, yttrium and the rare earths in silicate rocks. The best line-to-background ratios were achieved by arcing samples in a matrix of 4% sodium chloride in carbon powder. An atmosphere of 20% argon and 80% oxygen was used to reduce background and eliminate cyanogen band interference. An anion-exchange procedure was used to separate the rare earths from other elements. The resultant enrichment allowed use to be made of less sensitive rare earth lines in the ultraviolet end of the spectrum where the spectrographic dispersion is greater. Line interferences were studied and necessary corrections for these interferences were calculated The technique was tested by analysing the standard rocks, G-1, W-1 and CAAS syenite. Good agreement with recommended values was obtained

EMISSION SPECTROGRAPHY has been for many years one of the most satisfactory methods for the determination of rare earths in silicates.[1] Unfortunately, this technique suffers from several inherent disadvantages. These are: production of high background due to complex spectra of the rare earths; interference from titanium, iron and other rare earths; the necessity of high currents[2,3] and arcing times because of the relative involatility of the rare earth oxides. This latter factor also results in high background due to cyanogen emission in the range 3500–4200 Å where most of the useful analysis lines of the rare earths are found

Line interference may be reduced by use of a high-dispersion grating instrument and cyanogen emission may be controlled by arcing in various nitrogen-free atmospheres such as carbon dioxide,[4] argon, helium, oxygen,[5] and a mixture of argon and oxygen.[6,7,8] The use of a rare-gas atmosphere results in enhancement of ion line intensities relative to those of atom lines and an improvement of sensitivity due to the reduced background The main disadvantage is that arcing times of the order of minutes are required. Another approach to the problem of background is the carrier distillation method[7,9,10] which allows arcing times to be reduced by increasing volatilization rates. To obtain high-precision quantitative results, use of zirconium,[11] palladium,[12] and certain rare earths[1,13,14] as internal standards has been recommended.

The relatively high sensitivity of rare earth analysis referred to in the literature[1,15] was obtained *via* a high-dispersion instrument. The quantitative determination of yttrium, thorium and the rare earth elements with a large quartz spectrograph is extremely difficult because of the low dispersion of the instrument in the region where the analysis lines occur. This results in interference from major constituents of a rock

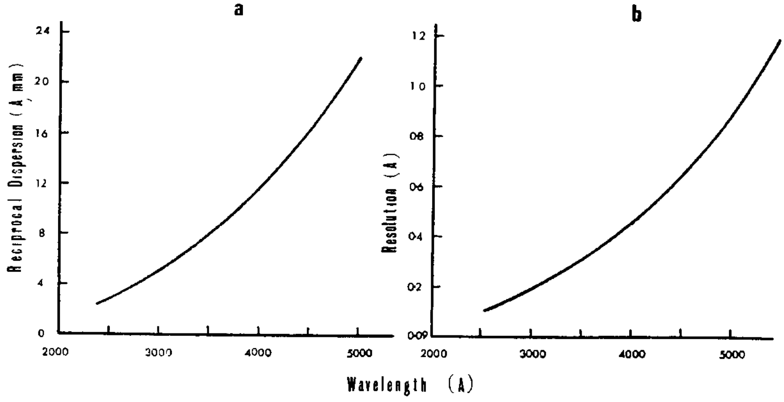

FIG 1. *a*. Reciprocal dispersion (Å/mm) as a function of wavelength (Å) for the Hilger E742 quartz-optics spectrograph.

b. Resolution (Å) as a function of wavelength (Å) for the same instrument.

sample, particularly from such elements as iron and titanium. Even when these elements have been removed, mutual interference still exists owing to the extremely complex spectra of yttrium, thorium and the rare earth elements.

Figure 1*a* shows the variation of reciprocal dispersion (Å/mm) as a function of wavelength (Å) and Fig. 1*b* shows the resolution of the instrument (Å) as a function of wavelength, for the Hilger E742 large automatic quartz-optics spectrograph. The method of determining the resolution is shown in the experimental section of this paper. A curve for a grating instrument is not shown in the figure, since the dispersion is constant at about 5·5 Å/mm for a 3·4-m instrument.

There is clearly a need for a method which will permit the use of a large quartz-optics instrument in rare earth determination. To achieve this aim it is essential to carry out a separation of yttrium, thorium and the rare earths from the major constituents of the sample to be analysed. The effect of such a separation is two-fold: not only are some line interferences removed, but also the enrichment effect enables use to be made of weaker rare earth lines in the ultraviolet end of the spectrum where the optical dispersion of the instrument is greater and where line interference is hence reduced.

Separation methods commonly used are: precipitation of rare earth elements as hydroxides[3] or oxalates,[4] solvent extraction[5,6,9,10,11] and ion-exchange.[16–21] Precipitation and solvent extraction techniques often prove unsuitable because of incomplete recovery. Cation-exchange usually involves large eluting volumes with a consequent reduction in the concentration of the analysis element.

Korkisch and Arrhenius[22] used anion-exchange to separate yttrium, thorium, uranium and the rare earths from macro-constituents. Carswell,[23] using anion-exchange, separated thorium from uranium, and Danon[24] separated some rare earth elements from thorium.

In the work described in this paper, a survey was made of the optimum conditions for the spectrochemical determination of thorium, yttrium and rare earth elements with a large quartz-optics spectrograph The survey includes observations on the effects of such variables as: gas conditions, carriers, currents and the selection of a suitable internal standard. Special attention was given to a study of mutual interferences of rare earth elements. Also, a suitable anion-exchange procedure is described for separation of thorium, yttrium, the rare earths and uranium from macro elements, followed by fractionation of thorium, yttrium and rare earths from uranium before their determination.

A combination of the anion-exchange separation and improved spectrochemical analysis allowed data for these elements to be obtained for the standard rocks G-1,[25] W-1[25] and CAAS syenite.[26]

Although this procedure was developed specifically for a large quartz instrument, it will also serve to improve analyses carried out with a grating spectrograph.

EXPERIMENTAL

Apparatus

The experiments were carried out on a Hilger E742 Large Automatic Spectrograph with quartz optics (reciprocal dispersion 12 Å/mm at 4000 Å). A Hilger microdensitometer with Galvoscale calibrated in B-values[27] was used for densitometry.

An image of the arc was focussed on the slit *via* a quartz spherical lens and the spectra were recorded on Ilford G-30 spectrographic plates developed for 4½ min in Kodak D19b developer at 20°.

Sample preparation

In all cases, solutions of rare earths, whether as ion-exchange eluates or as pure solutions for testing arcing conditions, were treated in the following standard manner.

A quantity of finely-divided carbon powder (50 mg) was added to not more than 50 ml of a solution of yttrium, thorium and rare earths contained in a 100-ml beaker. The carbon powder (120-mesh) contained an added internal standard. After addition of the required amount of carrier, the contents of the beaker were evaporated to dryness at 80° and the dry carbon powder was removed, ground in a mortar and loaded into graphite electrodes (cavity 6 mm deep and 1·5 mm bore) which were dried at 130° for 2 hr.

Choice of arcing conditions

Preliminary experiments with various arcing atmospheres such as carbon dioxide and varying proportions of an argon–oxygen mixture indicated that the best conditions for elimination of cyanogen interference bands and for the reduction of background were achieved with a mixture of 80% oxygen and 20% argon.

Use of carrier for improving sensitivities

An investigation was made of the variation of sensitivity with such variables as type of carrier, carrier concentration, arcing times and arcing currents. All experiments were carried out with an 80% oxygen–20% argon mixture.

Ahrens[1] divides the rare earths into three volatility groups. Representative elements (ytterbium, lanthanum, cerium, europium, holmium) from each of these three groups were taken as well as yttrium and thorium. Samples containing 100 ppm of each of these elements were prepared in matrices containing 2, 4 and 6% of the following carriers sodium chloride, sodium fluoride, caesium chloride, silver chloride. Samples without carrier were also prepared for comparison.

Volatilization curves were obtained for each sample at 8, 10, 12 and 14 A (d.c. arc with anode excitation).

Time for complete volatilization without carrier was 35 sec, whereas with carrier the time varied from 20 sec at 14 A to 30 sec at 8 A with all carriers and concentration ranges Line-to-background ratios were computed for each set of conditions and showed that all carriers increased the line-to-background ratio and improved the detection limit of each element

With each carrier, this effect usually increased to a maximum at 10 and 12 A, decreasing again at 14 A. It was observed that 4 and 6% sodium chloride at 10 and 12 A respectively provided the largest increase in line-to-background ratios and improvement in the detection limit for every element Results obtained for some representative elements under these conditions are shown in Table I

TABLE I.—LINE-TO-BACKGROUND RATIOS AND DETECTION LIMITS FOR HOLMIUM, YTTERBIUM AND THORIUM

Line, Å	Current, A	4% NaCl carrier A	4% NaCl carrier B	6% NaCl carrier A	6% NaCl carrier B	No carrier A	No carrier B
Ho 3456	10	9·6	1·5	9·5	3·0	2·2	9·0
	12	9·0	1·5	13·0	3·0	2·3	6·0
Yb 3289	10	32·0	0·6	36·0	0·6	4·2	5·0
	12	34·0	0·6	48·0	0·4	6·2	5·0
Th 4019	10	4·6	5·0	4·0	6·0	1·4	9.0
	12	3·5	5·0	3·2	5·0	1·4	9·0

A Line-to-background ratio.

B Approximate detection limit (ppm) as calculated from successive dilutions of standards and photometric measurements of line intensities.

Palladium and zirconium as internal standards

To investigate the suitability of palladium and zirconium as internal standards for yttrium, thorium and the rare earths, samples containing 100 ppm of each of these elements and 1000 ppm palladium and zirconium were prepared in carbon matrices containing 4 and 6% sodium chloride. Each sample at a particular concentration of carrier was arced at 10 and 12 A in the argon–oxygen atmosphere and successive exposures were made at 5-sec intervals In all cases, the volatilization behaviour of palladium more closely resembled that of yttrium, thorium and the rare earths than did that of zirconium, which required up to 15 sec longer for complete volatilization. The results also showed that in a sample containing 4% sodium chloride and arced at 10 A, the volatilization of palladium resembled that of yttrium, thorium and the rare earths more closely than under any of the other conditions employed Volatilization at 10 A with 4% sodium chloride was complete in under 25 sec. With palladium as internal standard, coefficients of variation ranged from ±6% for common elements such as lanthanum and cerium to ±15% for elements of low concentration such as samarium and lutecium.

Dissolution of rock samples

Concentrated nitric and concentrated hydrofluoric acids (15 ml of each) were added to 1 g of finely-divided rock sample (120-mesh) in a 250-ml teflon beaker and evaporated to dryness over a period of 2–3 hr. Then 15 ml of concentrated nitric acid were added to the residue, which was next transferred to a 150-ml glass beaker and slowly evaporated to dryness. To this residue were added 15 ml of a 9.1 mixture of glacial acetic acid and $5M$ nitric acid, and the whole was transferred to a tube and centrifuged. The supernatant liquid was retained and the residue was again treated with 15 ml of concentrated nitric acid, evaporated to dryness, taken up in 15 ml of the acetic acid–nitric acid mixture and centrifuged The solution was retained and the residue was dried, weighed, mixed in 1.3 ratio with sodium peroxide and fused in a platinum crucible at 480° for 7 min.[28] The melt was neutralized with nitric acid and the solution was centrifuged. Any solid remaining was discarded. Sufficient glacial acetic acid to give the correct ratio of acetic acid to nitric acid was added and all three supernatants were combined. The total volume was usually 70–80 ml.

Anion-exchange separation

The procedure used was a modification of work reported by Korkisch and Arrhenius [22] The method used was as follows.

A 150 × 10 mm column of Dowex 1 × 8 (100-mesh) in the nitrate form was initially equilibrated with 45 ml of the acetic acid–nitric acid mixture. The rock solution in the same medium was passed through the column at a flow-rate of 0·7 ml/min followed by 50 ml of the acid mixture to remove any weakly-adsorbed elements. Yttrium, thorium, uranium and the rare earth elements remained adsorbed on the resin.

Uranium was separated from thorium, yttrium and the rare earths by eluting with 35 ml of $6M$ hydrochloric acid This converted the uranium into its corresponding chloro-complex which remained adsorbed on the column, whereas yttrium, thorium and the rare earths were eluted as they do not form chloro-complexes at this acid strength. The uranium was eluted with 25 ml of $0{\cdot}1M$ hydrochloric acid and then determined fluorimetrically [29]

Mutual interference of yttrium, thorium and rare earth analysis lines

The resolution of the large quartz spectrograph was determined arbitrarily by use of the Hilger microdensitometer, with and without a chart recorder. The minimum distance between any two resolvable lines on the photographic plate was determined and found to be about 0·04 mm. With use of this value, Fig. 1*b* was obtained from Fig. 1*a*.

From these figures it is possible to calculate a potential interference band of wavelengths on either side of the analysis line, at different wavelengths. From the NBS tables,[30] possible interfering rare earth element lines may be found. The extent to which the elements interfere can be obtained approximately from the formula:

$$\%\ \text{Interference} = 100 \times \frac{A_i I_i}{A_a I_a}$$

where A_i, A_a are the respective abundances of the interfering and analysis elements and I_i, I_a are the respective line intensities.

It must be emphasised that if intensity values from the NBS Tables are used to compute this interference, the results may be different from those obtained with experimental conditions different from those used by the authors of these tables.

To check the validity of this formula under the conditions used, separate solutions were prepared from "Specpure" rare earth oxides for each interfering element. Samples containing 100 ppm of each element were prepared and arced under the standard conditions.

Results showed that for a predicted interference of up to 10%, no interfering line was detected in the spectrum of the rare earth element.

Table II lists the analysis lines used for yttrium, thorium and the rare earths with the respective interfering lines of other rare earth elements and intensity ratios for subsequent correction. The analysis lines tested are not always the recommended R.U. lines but in some cases are lines of lower wave-length which, although of lower sensitivity, may still be used because of the ion-exchange enrichment and separation procedure. The table does not list all the possible interfering lines as given in the NBS tables but only those which give an interference of more than 10% (considering the normal abundance ratios of these elements) as calculated by the formula and which were detectable in the spectrum of the pure element. In all cases, the highest likely concentration of the interfering element was taken in order to allow for the maximum interference possible.

When significant interferences are obtained, corrections are made as in the following example. As the neodymium line at 4040·80 Å interferes with the cerium line at 4040·76 Å, the intensity ratio

TABLE II —ANALYTICAL LINES AND INTERFERENCES

Analytical lines, Å (*intensities*)*	Interference range, Å (from Fig 1*b*)	Interfering lines, Å (*intensities*)*	Intensity ratios of interfering lines and reference correction lines
La 3995·75 (360)	±0·48	None	None
Ce 4040·76 (150)	±0·50	Nd 4040·80 (180)	Nd 4040/Nd 4061 = 0·732
Pr 4179·42 (460)	±0·55	Ce 4179·29 (5)	Ce 4179/Ce 4019 = 0·076
		Nd 4179·38 (38)	Nd 4179/Nd 4061 = 0·067
		Th 4179·71 (18)	Th 4179/Th 4019 = 0·051
Nd 4061·09 (280)	±0·50	None	None
Sm 4256·38 (140)	±0·59	Ce 4256·16 (12)	Ce 4256/Ce 4040 = 0·092
Eu 4205·05 (4000)	±0·57	None	None
Gd 3422·57 (700)	±0·30	None	None
Tb 3324·40 (400)	±0·27	None	None
Dy 3531·70 (2000)	±0·33	None	None
Ho 3456·00 (1800)	±0·31	None	None
Er 3692·64 (700)	±0·38	None	None
Tm 3462·20 (800)	±0·32	None	None
Yb 3289·37 (2600)	±0·27	None	None
Lu 2911·39 (600)	±0·18	Th 2911·32 (8)	Th 2911/Th 4019 = 0·027
Y 3327·89 (600)	±0·27	None	None
Th 4019·13 (300)	±0·50	Ce 4019·04 (14)	Ce 4019/Ce 4040 = 0·237
Pd 3421·24 (1400)†	±0·30	None	None

* Intensities from NBS Tables [30]

† Internal standard.

of the neodymium lines at 4040 and 4061 Å in the absence of cerium, was measured and found to be 0·732. The corrected cerium intensity at 4040·76 Å is obtained by subtracting 73% of the neodymium intensity at 4061·09 Å from the observed value for the cerium line.

The correction of analysis lines for interference should be carried out in the following sequence: correction of Ce 4040 for Nd 4040 interference is followed by correction of Th 4019 for Ce 4019, using the corrected Ce 4040 intensity value. The interference-free Ce 4040 and Th 4019 intensities having been obtained, Pr 4179 can be corrected for neodymium, cerium and thorium interferences. Working curves for interference-free elements can be prepared by dilution of a common mixed standard but other working curves must be prepared from individual unmixed standards.

RESULTS AND DISCUSSION

Experiments were carried out to test the recovery of elements from the ion-exchange column. Table III shows the results obtained for some representative elements. Analysis of the standard rocks G-1,[25] W-1[25] and CAAS syenite[26] for yttrium, uranium, thorium and the rare earths was carried out by the procedure developed. Table IV shows the results obtained.

Table III.—Recoveries from ion-exchange separations

Element	Added, μg	Recovered, μg
La	300	280
Ce	300	309
Nd	300	309
Sm	100	102
Eu	100	98
Gd	100	99
Dy	100	102
Ho	100	102
Y	100	100

Table IV.—Comparison of spectrographic, neutron-activation and recommended values for thorium, yttrium, uranium and the rare earths in G-1, W-1 and CAAS syenite

Element	G-1				W-1			CAAS Syenite		
	A	B	C	D	A	C	D	A	B	E
La	100	80	102	102	10	20	11·7	187	245	230
Ce	200	160	200	134	20	25	24	350	625	300–1100
Pr	19	16	17	20·9	5	4	3·68	137	140	<500
Nd	60	43	55	54·6	16	17	15·1	300	305	325
Sm	<5	<10	11	8·6	<5	5	3·79	<5	245	<100
Eu	0·9	1	1	1·04	1·5	1·1	1·09	15	8	<500
Gd	7	<10	5	4·88	4	4	4·2	72	48	150
Tb	<2	<50	0·6	0·5	<2	0·8	0·75	<2	<50	<100
Dy	2	<20	2	n.d.	2	4	n.d.	100	135	150
Ho	0·4	<1	0·5	0·5	3	1·2	1·35	21	2	<100
Er	1·4	<10	2	1·4	2·5	3	2·57	57	42	<50
Tm	<3	<1	0·2	0·2	<3	0·3	0·35	<3	5	<100
Yb	0·6	0·8	1	0·62	1·5	3	2·1	90	57	45–110
Lu	0·1	<10	0·15	0·17	0·3	0·3	0·33	1·5	<10	<100
Y	12	12	13	12·5	11	25	23·8	450	450	500
Th	30	21	52	n.d.	1	2·4	n.d.	710	1300	1400
U	2·6	<50	3·7	n.d.	1·5	0·5	n.d.	595	2700	2500

A—This work.
B—Tennant and Fellows[31] (direct arcing with high-dispersion instrument).
C—Fleischer[25] (recommended values for G-1 and W-1).
D—Haskin and Gehl[32] (neutron activation).
E—Webber[26] (recommended values for CAAS syenite).
n.d.—Not determined.

The agreement between the spectrographic results obtained by us for G-1 and CAAS syenite and those obtained by Webber[26], and Tennant and Fellows[31] is very good. Agreement with the recommended values of Fleischer[25] and particularly the neutron-activation data of Haskin and Gehl[32] for G-1 and W-1, is excellent.

It is concluded that the results in Table IV have demonstrated the possibility of using a large quartz-optics spectrograph for the determination of yttrium, thorium and the rare earths provided that an initial separation is carried out. The method should also prove helpful for analyses carried out with a high-dispersion instrument.

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Zusammenfassung—Die optimalen Bedingungen beim Einsatz eines großen Quarzspektrographen zur Bestimmung von Thorium, Yttrium und den seltenen Erden in Silikatgesteinen wurden aufgesucht. Die besten Verhaltnisse von Linien zum Untergrund wurden beim Abfunken der Proben in einer Matrix von 4% Natriumchlorid in Kohlepulver erreicht. Zur Ausschaltung von Dicyan-Banden und zur Verminderung des Untergrundes wurde eine Atmosphare von 20% Argon und 80% Sauerstoff verwendet. Die seltenen Erden wurden uber ein Anionenaustauschverfahren von anderen Elementen abgetrennt. Die dadurch erzielte Anreicherung erlaubte die Verwendung weniger empfindlicher Linien der seltenen Erden am ultravioletten Ende des Spektrums, wo die Dispersion großer ist Storungen der Linien wurden untersucht und die notwendigen Korrekturen für diese Storungen berechnet. Das Verfahren wurde durch Analyse der Standardgesteine G-1, W-1 und CAAS-Syenit gepruft.

Résumé—On a mené des études sur les conditions optimales d'emploi couronné de succès d'un spectrographe à grand quartz pour le dosage du thorium, de l'yttrium et des terres rares dans les roches aux silicates. Les meilleurs rapports raie à fond ont été réalisés en traitant les échantillons dans une matrice de 4% de chlorure de sodium dans la poudre de carbone On a utilisé une atmosphère de 20% d'argon et 80% d'oxygène pour réduire le fond et eliminer l'influence de la bande de cyanogène. On a utilisé une technique d'échange d'anions pour séparer les terres rares d'autres éléments. L'enrichissement résultant a permis l'utilisation de raies moins sensibles des terres rares dans l'extrêmité ultra-violette du spectre où la dispersion spectrographique est plus grande On a étudié les interférences de raies et calculé les corrections nécessaires pour ces interférences La technique a été essayée en analysant les roches étalons G-1, W-I et syénite CAAS. On a obtenu un bon accord avec les valeurs recommandées.

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POLAROGRAPHIC STUDY OF THE SUBSTITUTION REACTIONS OF THE CHELATES OF TRIETHYLENETETRAMINEHEXA-ACETIC ACID—I

REACTION OF THE ZINC CHELATE WITH CALCIUM IONS

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Summary—The mechanism of the substitution reaction between the binuclear zinc-triethylenetetraminehexa-acetic acid (TTHA) chelate (Zn_2X^{2-}) and calcium ions was studied by the polarographic technique. The results obtained under equilibrium and kinetic conditions permitted formulation of the reaction mechanisms as

$$Zn_2X^{2-} + Ca^{2+} + 4NH_3 \rightleftharpoons ZnXCa^{2-} + Zn(NH_3)_4{}^{2+}$$
$$Zn_2X^{2-} + 2Ca^{2+} + 8NH_3 \rightleftharpoons Ca_2X^{2-} + 2Zn(NH_3)_4{}^{2+}$$
$$Ca_2X^{2-} + 2Zn(NH_3)_4{}^{2+} \rightleftharpoons ZnXCa^{2-} + Zn(NH_3)_4{}^{2+} + 4NH_3$$

depending on the ratio Zn:Ca in the system studied The reaction studied proceeds only in the presence of ammonia. When calcium is replaced with a metal which has a TTHA chelate more stable than Zn_2X^{2-}, the mixed binuclear chelate is not formed.

ELECTROPHILIC substitution reactions of the chelates of the EDTA type are often studied in detail, in connection with analytical applications,[1–4] examination of the kinetics and mechanism,[5–8] or determination of stability constants.[9–12] Spectrophotometric methods are frequently used, but the polarographic technique[8,9,13–16] can also be applied because the measurement of the polarographic current does not influence the establishment of the substitution equilibrium. This paper presents the results of polarographic study of the reaction of zinc(II) chelates of triethylenetetraminehexa-acetic acid (TTHA)[17–21] with calcium ions. The corresponding substitution reactions involving EDTA[1,2] or EGTA[22] chelates are well known and have been used analytically.

In the system containing TTHA, zinc and calcium ions, the mechanism of the substitution differs from that for EDTA or EGTA chelates.

EXPERIMENTAL

Reagents

All solutions were prepared from reagent-grade chemicals The zinc solution was standardized by amperometric and visual titration with EDTA. Other metal salt solutions were also standardized with EDTA titrations. TTHA solution (0 01*M*) was standardized by visual titration with zinc solution.[23]

Apparatus

Polarographic measurements were performed with a Metrohm Polarecord E 261 R, using an H-type polarographic cell with a separate saturated calomel electrode. The temperature of polarographed solutions was kept constant at 22° in a thermostat.

Procedure

The concentration of non-chelated zinc(II) ions in the system Zn–TTHA–Ca was measured polarographically. Because the zinc-TTHA chelates are polarographically inactive[24] the method of measurement was as follows. First the height of the zinc wave was measured in the absence of TTHA. After the addition of TTHA the height of the wave decreased. Addition of calcium resulted in the release of zinc ions and the height of the measured wave again increased. This increase was measured as a function of time, till a constant value was reached.

RESULTS AND DISCUSSION

Preliminary measurements

First the formation of the Zn_2X^{2-} chelate (H_6X = TTHA) in ammoniacal solution was verified by amperometric titration. The height of the zinc wave decreased, becoming zero at the molar ratio Zn:TTHA = 2:1. Further addition of ligand did not alter the shape of the polarographic curve. Preliminary measurement in the Zn–TTHA–Ca system showed that the release of zinc(II) ions from the Zn_2X^{2-} chelate takes place only in media containing ammonia. The displacement of zinc was found to be time-dependent, the rate of the reaction depending on Zn:Ca ratio and the concentration of ammonia. When the ratio Zn:TTHA:Ca was 2:1:1, the amount of zinc ions released was 50% of the initial concentration of zinc. This led to the hypothesis that under given conditions a mixed binuclear chelate $ZnXCa^{2-}$ can be formed in the system studied.

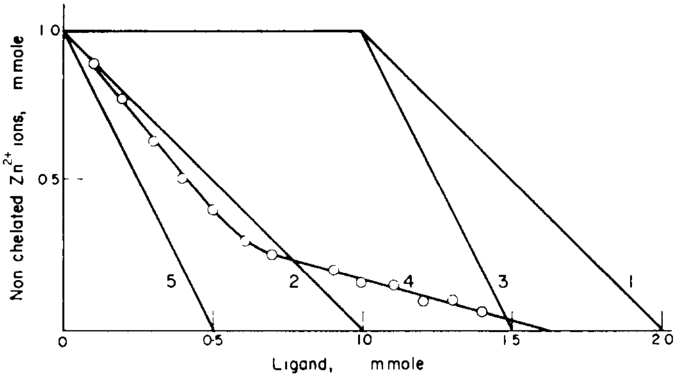

FIG. 1.—Amperometric titrations of 1:1 mixture of zinc and calcium ions with TTHA.

1. Theoretical titration curve if only CaX^{4-} and ZnX^{4-} are formed.
2. Theoretical titration curve if only $ZnCaX^{2-}$ is formed.
3. Theoretical titration curve if only CaX^{4-} and Zn_2X chelates are formed.
4. Experimental titration curve.
5. Theoretical titration curve for the titration of Zn with TTHA.

This hypothesis was first tested experimentally by amperometric titration with TTHA of an equimolar mixture of calcium and zinc, the concentration of non-chelated zinc ions being measured. The shape of the titration curve depends on the mechanism of formation of the chelates involved. If only the binuclear chelate $ZnXCa^{2-}$ is formed during the titration, the resulting titration curve should be as shown in Fig. 1, curve 2. If no binuclear chelate is formed (only CaX^{4-} and ZnX^{4-} chelates successively formed), the curve should have the shape found for titration with EDTA,[25,26] of a mixture of zinc and calcium ions see Fig. 1, curve 1. If, on the other hand, only the chelates CaX^{4-} and Zn_2X^{2-} were successively formed, the resulting titration curve should be as shown in Fig. 1, curve 3. Titration of zinc ions alone gives curve 5 in Fig. 1. The experimental curve for titration of an equimolar mixture of zinc and calcium ions is given as curve 4 in Fig. 1. Similar curves were obtained for titration of zinc and calcium in various ratios.

In all these titrations the total consumption of the titrant showed the formation of CaX^{4-} and Zn_2X^{2-} chelates, but the course of the titration curve suggested a more complicated reaction mechanism. The experimental curve can be interpreted as follows. At the beginning of the titration the mixed binuclear $ZnXCa^{2-}$ chelate is formed nearly quantitatively, owing to the large excess of both metals relative to the ligand. This part of the curve should therefore closely follow curve 2 in Fig. 1. During further addition of ligand the most stable chelate should form, Zn_2X^{2-}, but the free calcium ions may displace zinc from this chelate. The resultant effect will be that the concentration of non-chelated zinc ions will be lower than that for formation of mixed binuclear chelate only, but higher than that for formation of the Zn_2X^2 chelate only. In the region just before the end-point of the titration the concentration of the titrant is so high that the relatively labile $ZnXCa^{2-}$ chelate dissociates and the resulting products are Zn_2X^{2-} and CaX^{4-}.

Reaction between Zn_2X^{2-} *chelate and calcium ions*

Equilibrium study. The curve for calcium and zinc titrated with TTHA showed some evidence of the formation of the mixed binuclear chelate $ZnXCa^{2-}$. The exchange reaction was therefore formulated as

$$Zn_2X^{2-} + Ca^{2+} + 4NH_3 \rightleftharpoons Zn(NH_3)_4{}^{2+} + ZnXCa^{2-} \qquad (1)$$

Because the mixed chelate is expected to be not very stable, reaction (1) is probably valid only for certain Zn:Ca ratios. Under optimum conditions, the validity of reaction (1) can be verified by calculation of the equilibrium constant K_1, defined as

$$K_1 = \frac{[Zn(NH_3)_4{}^{2+}][ZnXCa^{2-}]}{[Zn_2X^{2-}][Ca^{2+}][NH_3]^4} \qquad (2)$$

To obtain the data for the calculation of K_1, a series of measurements was carried out as described under *Procedure*, with $1{\cdot}0 \times 10^{-4}M$ zinc and $0{\cdot}5 \times 10^{-3}M$ TTHA and the calcium concentration varied from 0 to $2{\cdot}0 \times 10^{-3}M$, in solutions with various concentrations of ammonia. The concentration of zinc ions released was determined under equilibrium conditions, 10 min after mixing of the components.

The results are presented in Fig. 2. It is evident that in the ammonia concentration range 2–6*M*, the course of the reaction was practically uninfluenced by the concentration of ammonia, and that one equivalent of calcium was enough to release one equivalent of zinc. The results obtained suggest that the reaction mechanism is well expressed by reaction (1) which in turn can be expressed as two simultaneous reactions

$$Zn_2X^{2-} + Ca^{2+} \rightleftharpoons ZnXCa^{2-} + Zn^{2+} \qquad (3)$$

$$Zn^{2+} + 4NH_3 \rightleftharpoons Zn(NH)_4{}^{2+} \qquad (4)$$

To reactions (3) and (4) correspond the equilibrium constants K_2 and K_3, defined as

$$K_2 = \frac{[ZnXCa^{2-}][Zn^{2+}]}{[Zn_2X^{2-}][Ca^{2+}]}$$

$$K_3 = \frac{[Zn(NH_3)_4{}^{2+}]}{[Zn^{2+}][NH_3]^4}$$

The equilibrium constant K_1 of reaction (1) is therefore given by

$$K_1 = K_2K_3 . \tag{5}$$

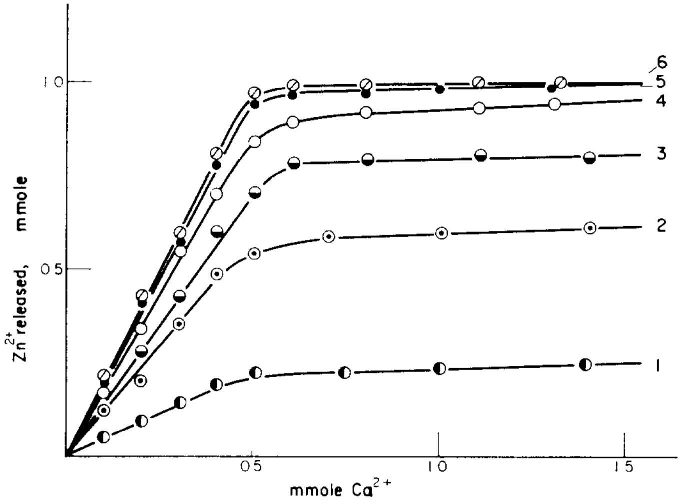

FIG 2.—Displacement of Zn^{2+} ions from the Zn_2X^{2-} chelate with Ca^{2+} ions as a function of added $[Ca^{2+}]$ and $[NH_3]$.
Ammonia concentration: *1*—0·3*M*; *2*—0·6*M*; *3*—0·9*M*, *4*—1·4*M*; *5*—2*M*; *6*—6*M*.

The total concentrations of zinc, C_{Zn}, calcium, C_{Ca}, ligand, C_X, and ammonia, C_A, are defined as

$$C_{Zn} = 2[Zn_2X^{2-}] + [ZnXCa^{2-}] + [Zn^{2+}] + [Zn(NH_3)_4{}^{2+}] \tag{6}$$

$$C_{Ca} = [Ca^{2+}] + [ZnXCa^{2-}] \tag{7}$$

$$C_X = [Zn_2X^{2-}] + [ZnXCa^{2-}] \tag{8}$$

$$C_A = [NH_3] + 4[Zn(NH_3)_4{}^{2+}] \tag{9}$$

During all measurements C_{Zn} was twice C_X. Combination of equations (6) and (8) with K_3 and $C_{Zn} = 2C_X$ gives $[ZnXCa^{2-}]$:

$$[ZnXCa^{2-}] = a\left(1 + \frac{1}{K_3[NH_3]^4}\right) \tag{10}$$

where a is the concentration of $Zn(NH_3)_4{}^{2+}$ determined polarographically.

Substituting equation (10) into equation (8) gives

$$[Zn_2X^{2-}] = C_X - a\left(1 + \frac{1}{K_3[NH_3]^4}\right) \tag{11}$$

Similarly, from equation (7),

$$[\mathrm{Ca}^{2+}] = C_{\mathrm{Ca}} - a\left(1 + \frac{1}{K_3[\mathrm{NH}_3]^4}\right) \tag{12}$$

Further substitution of relations (10), (11) and (12) into equation (2) gives the expression for K_1:

$$K_1 = \frac{a^2\left(1 + \dfrac{1}{K_3 C_A{}^4}\right)}{\left\{C_X - a\left(1 + \dfrac{1}{K_3 C_A{}^4}\right)\right\}\left\{C_{\mathrm{Ca}} - a\left(1 + \dfrac{1}{K_3 C_A{}^4}\right)\right\} C_A{}^4}, \tag{13}$$

C_A being used instead of the concentration of free ammonia because the error is very small if the concentration of ammonia is relatively high (0·5–5·0*M*) and the concentration of zinc ions very small ($10^{-3}M$). [See equation (9)].

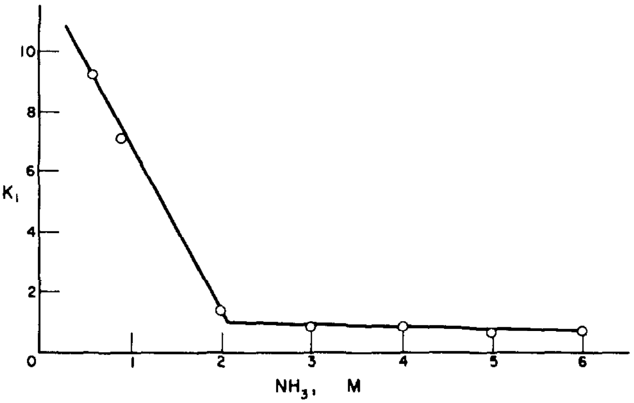

FIG. 3 —Dependence of the value of the equilibrium constant K_1 on the concentration of ammonia.

The values of K_1 calculated according to equation (13) are presented as a function of ammonia concentration in Fig. 3, which shows that the equilibrium constant K_1 has an almost constant value for the concentration range of ammonia from 2 to 6*M*, the deviation from constancy probably being due to the fact that the equilibrium $NH_3 + H^+ \rightleftharpoons NH_4{}^+$ was ignored. The low stability of the mixed binuclear chelate $ZnXCa^{2-}$ is in good agreement with the interpretation of the titration curves. The quantitative treatment of the exchange equilibrium also confirmed the validity of reaction (1).

Kinetic study. Kinetic experiments on the system Zn–Ca–X–NH_3 were done with variation in the concentration of one component at a time. The non-chelated zinc ion concentration was measured polarographically as before. The results showed that the exchange reaction between calcium ions and Zn_2X^{2-} chelate was first-order with respect to both reactants. These findings agree with earlier studies of the exchange reactions of many EDTA chelates [6,13,14,27,28] The concentration of calcium ions was varied from $3{\cdot}0 \times 10^{-4}M$ to $1{\cdot}0 \times 10^{-2}M$ at constant zinc concentration $1{\cdot}0 \times 10^{-3}M$. As the calcium concentration was increased, the kinetic dependence on it changed from first-order to zero-order and back again to first-order, zero-order being found at the ratio Zn:Ca:X = 2:1:1. At a very high concentration of calcium (more than corresponded to the ratio Zn:Ca = 1:10) the kinetic dependence probably changed again from first-order to zero-order. The results are plotted in Fig. 4. Changes of reaction order are well-known in organic systems[29] and have also been observed in the dissociation of nickel–ethylenediamine complexes[30] and the substitution reaction of copper ions with nickel–EDTA chelate.[31]

In the reaction studied, the first change of the reaction order appears to be due only to the shift of the relative concentrations without any change in the nature of the reactants. This means that the ratio Zn:Ca:X = 2.1:1 represents the optimum conditions for the formation of the $ZnXCa^{2-}$ chelate. Under these conditions the reaction of Zn_2X^{2-} chelate with calcium ions can therefore be formulated by reaction (1). This formulation is valid only for small concentrations of calcium, not exceeding the ratio Zn:Ca = 2:1. At a higher concentration of calcium the exchange reaction should be expressed as

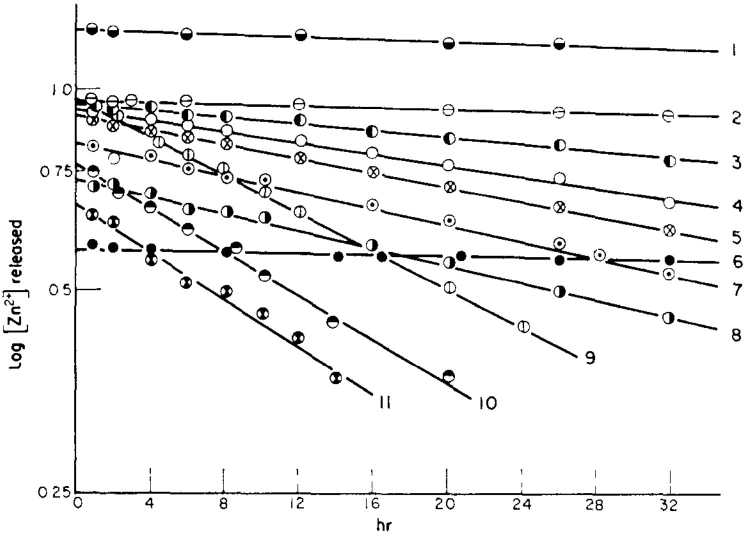

FIG. 4.—Time dependence of the concentration of released Zn^{2+} ions at various Zn Ca ratios and NH_3 concentrations
1—Zn.Ca = 3:2, NH_3 = 3·3*M*; *2*—Zn Ca = 1 10, NH_3 = 3·3*M*; *3*—Zn·Ca = 1:5, NH_3 = 3·3*M*; *4*—Zn·Ca = 1·5, NH_3 = 2 2*M*; *5*—Zn:Ca = 1 5, NH_3 = 1·1*M*; *6*—Zn·Ca = 2 1, NH_3 = 3·3*M*; *7*—Zn:Ca = 1:1, NH_3 = 3·3*M*; *8*—Zn:Ca = 1 1, NH_3 = 2·2*M*; *9*—Zn:Ca = 1 2, NH_3 = 3 3*M*; *10*—Zn Ca = 1.2, NH_3 = 1·1*M*; *11*—Zn.Ca = 1.1, NH_3 = 1.1*M*;

$$Zn_2X^{2-} + 2Ca^{2+} + 8NH_3 \rightleftharpoons Ca_2X^{2-} + 2Zn(NH_3)_4{}^{2+}$$

$$Zn(NH_3)_4{}^{2+} + Ca_2X^{2-} \rightleftharpoons ZnXCa^{2-} + 4NH_3 + Ca^{2+}$$

At a high concentration of calcium the formation of the mixed binuclear chelate is practically completely inhibited and only the first of these reactions takes place.

The concentration of ammonia influenced the exchange rate, the rate generally decreasing with increasing concentration of ammonia, but did not influence the nature of the exchange process.

Reaction of the ZnX^{4-} *chelate with calcium ions*

The reaction of the ZnX chelate with calcium ions was not examined in detail, but only sufficiently to obtain the necessary information for comparison with the reaction of the Zn_2X chelate. The measurement was carried out under equilibrium conditions: the amount of released zinc ions was measured polarographically after the addition of each fraction of calcium salt. The concentration of zinc was measured at intervals of time until it reached a constant value. Figure 5 illustrates the different courses of the reactions of ZnX and Zn_2X chelates. Even in the case of the ZnX chelate the results did not suggest a simple exchange of one zinc ion by one calcium ion as observed for the reaction of the Zn–EDTA chelate with calcium. For interpretation, the formation of some mixed chelate should be taken into account, as in the case of the Zn_2X chelate. The polarographic method however, did not yield all the data needed.

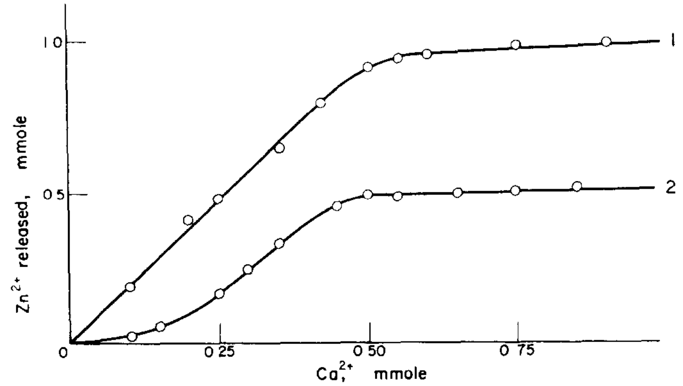

FIG. 5 —Displacement of Zn^{2+} ions from the Zn_2X^{2-} and ZnX^{4-} chelates with calcium dependence on the amount of added Ca ions.
1. Zn_2X^{2-} chelate in 2*M* NH_3.
2. ZnX^{4-} chelate in 2*M* NH_3.

Reactions of the Zn_2X^{2-} *chelate with other cations*

To establish how the exchange reaction was influenced by the stability of the TTHA chelate of the metal used for displacement, some other cations not forming complexes with ammonia were examined. When calcium was replaced by a similar cation with a slightly less stable TTHA chelate, *e.g.*, magnesium or barium, the reaction mechanism was similar. With a metal which had a TTHA chelate with high stability relative to the calcium chelate) a completely different reaction mechanism was observed. A suitable metal was lanthanum,[19] ($\log K_{LaX} = 23{\cdot}1$, $\log K_{La_2X} = 26{\cdot}9$). With the experimental techniques described above, a relatively simple reaction was observed between lanthanum ions and the Zn_2X chelate:

$$Zn_2X^{2-} + 2La^{3+} + 8NH_3 \rightleftharpoons La_2X + 2Zn(NH_3)_4{}^{2+}$$

CONCLUSION

The exchange reaction between calcium ions and the binuclear zinc–TTHA chelate in ammoniacal medium has a different mechanism from that for EDTA chelates.

The presence of ammonia is necessary for the release of zinc ions from the Zn_2X chelate. The role of ammonia in the system may be formally compared to the dissociation of EDTA chelates in acidic media, in the exchange reaction of these chelates. Here the dissociation is the first step of (in some cases) a very complicated reaction mechanism which results in a complete exchange of both metal ions involved. Before the second metal ion reacts with the EDTA chelate, the dissociation of this chelate may be practically complete[31] in acidic solution. Most probably this is not the case when calcium ions react with binuclear Zn–TTHA chelate in ammoniacal solution. The tendency of ammonia to form stable complexes with zinc should be taken into account. The attack of calcium ions on the nitrogen–zinc bond in the Zn_2X^{2-} ion may occur only with simultaneous action by ammonia, which does not itself break the nitrogen–zinc bond, but most probably makes it weaker.

The experiments in which a metal other than calcium was used suggests that the formation of a mixed binuclear chelate takes place only when the Zn_2X^{2-} chelate reacts with a cation which forms a TTHA chelate much less stable than the Zn_2X^{2-} chelate.

Contrary to the existence of a binuclear chelate observed in the study of the exchange reaction of EDTA chelates,[31] the mixed binuclear chelate of TTHA is not an unstable reaction intermediate, but—under optimum conditions—a product of the exchange reaction. This can be explained in terms of steric factors; TTHA has 10 donor groups which geometrical considerations show are available for 1, 2 or even 3 metal ions.[19,20,24]

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Zusammenfassung—Der Mechanismus der Substitution des zweikernigen Zink-Triathylentetraminhexaessigsaure-(TTHA-)Chelats (Zn_2X^{2-}) durch Calciumionen wurde polarographisch untersucht. Die im Gleichgewicht und unter nichtstationaren Bedingungen erhaltenen Ergebnisse erlauben die Formulierung des Reaktionsmechanismus als

$$Zn_2X^{2-} + Ca^{2+} + 4NH_3 \rightleftharpoons ZnXCa^{2-} + Zn(NH_3)_4{}^{2+},$$
$$Zn_2X^{2-} + 2Ca^{2+} + 8NH_3 \rightleftharpoons Ca_2X^{2-} + 2Zn(NH_3)_4{}^{2+},$$
$$Ca_2X^{2-} + 2Zn(NH_3)_4{}^{2+} \rightleftharpoons ZnXCa^{2-} + Zn(NH_3)_4{}^{2+} + 4NH_3,$$

je nach dem Zn:Ca-Verhaltnis im untersuchten System Die untersuchte Reaktion lauft nur in Gegenwart von Ammoniak ab. Wird Calcium durch ein Metall mit stabilerem TTHA-Chelat als Zn_2X^{2-} ersetzt, so bildet sich kein gemischt zweikerniges Chelat.

Résumé—On a étudié le mécanisme de la réaction de substitution entre le chélate binucléaire zinc–acide triéthylènetétraminohexacétique (TTHA) (ZnX^{2-}) et les ions calcium par la technique polarographique. Les résultats obtenus dans des conditions d'équilibre et de cinétique permettent de formuler les mécanismes des réactions comme suit:

$$Zn_2X^{2-} + Ca^{2+} + 4NH_3 \rightleftharpoons ZnXCa^{2-} + Zn(NH_3)_4{}^{2+}$$
$$Zn_2X^{2-} + 2Ca^{2+} + 8NH_3 \rightleftharpoons Ca_2X^{2-} + 2Zn(NH_3)_4{}^{2+}$$
$$Ca_2X^{2-} + 2Zn(NH_3)_4{}^{2+} \rightleftharpoons ZnXCa^{2-} + Zn(NH_3)_4{}^{2+} + 4NH_3$$

selon le rapport Zn:Ca dans le système étudié. La réaction étudiée ne se développe qu'en présence d'ammoniaque. Lorsque le calcium est remplacé par un métal qui a un chélate TTHA plus stable que Zn_2X^{2-}, le chélate binucléaire mixte ne se forme pas

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PHOTOMETRIC TITRATIONS—XII*

A FULL-IMMERSION SPECTROPHOTOMETER

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Summary—A design for a photometric titration apparatus is described which includes facilities for variable path-length, zero suppression and scale expansion. The instrument may also be used as a simple spectrophotometer.

THE qualitities desired for a versatile, rugged, highly stable photometric titrator have been discussed in a previous paper[1] in which their partial realization in a semi-immersion phototitrator was shown. It was indicated that the design was a prototype for use while the full-immersion phototitrator was being developed. The work of designing and constructing a full-immersion phototitrator has been completed and is reported here.

Several full-immersion instruments have been described in the literature. Agazzi and Bond[2] reported a design in which two tubes are immersed in the solution. One tube contains the light source near the immersed end. A beam from this source passes through the solution to the immersed end of the other tube which contains the photoreceptor. A filter can be positioned in the light-path to select the appropriate wavelength. The length of the light-path is fixed, the light probe is sizable, and thus titrations of small samples become difficult.

The phototitrator by Fisher[3] immerses two light-conducting glass rods in the solution. Light leaves one rod, passes through a gap filled with the solution to be titrated, enters the other rod and is brought by it to the detector. The path-length is fixed, as in the preceding instrument, and some exclusion of external light is necessary. However, the use of an interference filter wedge, which allows continuous selection of the wavelength, is an improvement.

The best of the instruments so far described seems to be the Spectrosyn Electronic Colorimeter.[4] The light probe in this instrument is of quite small diameter and contains a small bulb enclosed in a cylindrical stainless-steel housing. This lamp housing and a second cylinder containing the photoreceptor are mounted on a steel rod. The light housing can be moved axially relative to the receptor compartment and thereby the path-length can be adjusted between 0 and 5 cm. The lamp is operated by a current pulsating at a frequency of 33·3 Hz. The signal due to the modulated light is isolated electronically from that due to the external light and rectified by a lock-in amplifier circuit. The resulting d.c. signal is displayed on a meter that reads in % transmittance. Thus external light need not be excluded. Monochromacy is achieved by small, specially mounted filters that are slipped onto the front plate of the detector

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* Part XI: *Talanta*, 1965, **12**, 913,

housing. Continuous wavelength variation is not possible. The instrument is mains-operated and thus subject to mains voltage fluctuations. Isolation of the a c. component in the detector output, and rectification, requires moderately sophisticated electronic circuity. However, two main requirements for an ideal phototitrator namely, variable path-length and independence of ambient light, are fulfilled in this design. An instrument of this type has been in use in the present authors' laboratory for several years, and has performed extremely well as a phototitrator. The limited precision (1 % transmittance according to the manufacturer) and influence of moderate mains voltage fluctuations are not serious in titrations in which enough readings are taken to provide an error-reducing averaging process.

Recently Muto and co-workers[5] reported on a "dipping colorimeter." The path-length is fixed, glass filters are used to achieve monochromacy and external light must be excluded.

DESIGN AND CONSTRUCTION

This work was directed toward the incorporation of the following design features: (1) variable path length, (2) continuous selection of wave length, (3) independence of ambient light, and (4) simplicity in electric circuitry.

Point 3 presented no problem since application of the principle of geometric exclusion of external light by use of a photodetector of extremely small sensitive area had already been demonstrated in previous designs [1,6] The application of such a detector automatically solves point 4, since a quite simple circuit consisting of only a few batteries, resistors and switches can be employed. Point 2 was solved by abandoning filters and operating with a grating. The construction of this portion of the optical part of the titrator was greatly facilitated by employing the collimating system and the grating with its drive mechanism from a Bausch and Lomb Spectronic 20. Development of an uncomplicated light probe that allows variation of the path-length presented the greatest difficulties in design and construction.

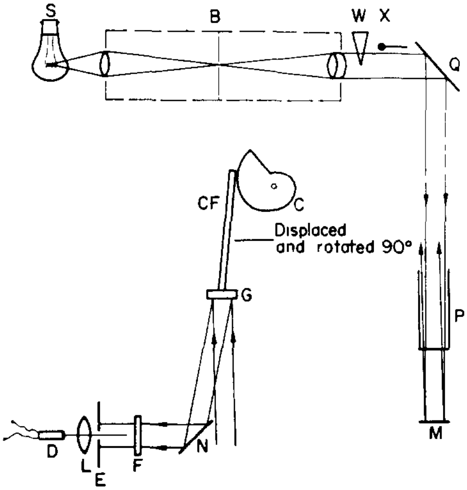

FIG. 1.—Schematic optical diagram.
B, lens assembly; *C*, cam; *CF*, cam follower; *D*, detector; *F*, infrared filter; *G*, grating; *L*, focusing lens; *M*, stage mirror; *N* and *Q*, mirrors; *P*, probe; *S*, exciter lamp, *W*, comb; *X*, shutter.

The general lay-out of the instrument is shown in Fig. 1. The light source, *S*, is a General Electric #209 automobile lamp. Light from the source is collimated by the lens assembly, *B*. This unit was taken intact from a Bausch and Lomb Spectronic 20, and consists of two lenses and a slit which serves as entrance slit for the monochromator. The collimated beam is reflected by a mirror, *Q*, down the probe assembly, *P*, which ends in a glass window. A second-surface mirror, *M*, is positioned in the sample solution below the end of the tubular probe. The light, after leaving the probe, is reflected by *M* back into the probe at an angle of 5 5°. When the probe assembly is submerged in a solution, the light beam returning to the probe from *M* has traversed the solution with a path-length of essentially twice the distance between the surface of the end window and the front surface of the mirror.

After having crossed the sample gap and traversed the tube again the light beam strikes a diffraction grating, *G*. This is a replica grating taken from a Bausch and Lomb Spectronic 20. It has been remounted to conform to the geometry of the optical path, but is driven by the cam, *C*, and cam-follower, *CF*, which accompany it in the Spectronic 20. It should be noted that Fig 1 has been drawn with the optical path broken and the grating and following optics displaced and rotated 90° from their orientation in the instrument. The diffracted light is directed by mirror *N* through an infrared filter, *F*, to the monochromator exit slit, *E*. Then the light is focused by lens *L* onto detector, *D*

The detector is a Texas Instrument IN2175 symmetrically diffused silicon photo-duo-diode, which is particularly suited for this application because of its small size and limited angle of acceptance of incident light. The device is only 12 mm in length by 2 mm in diameter. The light-sensitive area is less than 1 mm^2. The extremely small angle of acceptance for incident light is achieved by a lens which comprises the open end of the detector. The light-sensitive semiconductor chip is located at the focal point of this lens. Light off the optical axis misses the chip entirely. The spectral sensitivity of the device is adequate throughout most of the visible range but falls very rapidly at wavelengths below 420 mm. This fact, combined with reduced energy output by the light source at the shorter wavelengths, severely curtails exploitation of the near-ultraviolet region. The detector has its maximum sensitivity at about 10^{-6} m. The high sensitivity in this region makes necessary the infrared filter *F*, and this serves to eliminate the effect of overlapping spectra produced by the grating. Recently, a Texas Instrument LS-400 silicon photo-duo-diode has been used which is physically similar to the IN2175, but has about ten times greater sensitivity [7]

Two control devices are included in the optical path, a shutter, *X*, to completely block the light beam, both as protection for the detector and as zero transmittance reference, and a comb, *W*, for fine adjustments of the intensity of the incident light.

The titrator is completely contained in an aluminium box, 20 × 20 × 45 cm, especially assembled for the purpose. The box is divided down the long dimension into two compartments. One half contains the optical components, the other the electric circuitry All controls are grouped on or near the front panel for ease of operation. To facilitate repair and adjustment, the top, side and rear panels of the box are demountable and the front panel consists of two sections of which the right one is hinged. Connections to the galvanometer and exciter battery are made through pronged plugs mounted on the rear of the case. When in use, the instrument rests on a four-legged aluminium rack. This positions the titrator with the probe assembly several cm above the bench top, allowing room for a beaker and stirrer.

Figure 2 shows the arrangement of optical components in the box. The source, *S*, is mounted on a stage which is adjustable in all three dimensions. The source on the stage can also be axially rotated to achieve proper position of the lamp filament. Screw drive is provided for these adjustments, and set-screws allow locking. The collimating system, *B*, is permanently attached to the frame of the box as are the mounts for all other optical components. Controls for comb, *W*, and for shutter, *X*, are located on the side near the front of the box. The comb is driven by a worm gear, and the shutter is operated by a brass rod. Adjusting screws are provided for the optical alignment of mirrors *Q* and *N* as well as the stage for mirror, *M*. Alignment of detector, *D*, is also possible.

Detector, *D*, collimating lens, *L*, exit slit, *E*, and infrared filter, *F*, are mounted as a unit in an aluminium block, *DE*. The details of this unit are shown in the inset of Fig. 2. The permanent alignment of this group of components facilitates instrument alignment. In addition, the massive aluminium mount serves as a heat sink for the photoreceptor.

The probe assembly used for photometric titrations (see Fig. 2) consists of a 15-mm o.d. glass tube closed with a glass window at the lower end, and mounted in a 25-mm brass sleeve. The sleeve in turn fits snugly into an aluminium block which is secured to the phototitrator frame. Also mounted in this block are four stainless-steel rods These extend parallel to the probe, and below it, to the corners of a 3-cm square stainless-steel plate on which is mounted the mirror, *M*. The size of the stage is ample to accommodate both the stage mirror (12 × 9 mm) and a small magnetic stirring bar. The exposed portions of the stage and the support rods may be Teflon coated. The mounting of the support rods allows their exposed length to be adjusted and fixed by set-screws. Rough alignment of the optical path is achieved by adjusting stage orientation. Precise alignment is accomplished by using mirrors *Q* and *N*.

Variation of the path-length is achieved by driving the sleeve and the attached dipping glass tube with a rack and pinion gear. The rack is secured to the sleeve and the pinion gear to the mount. A

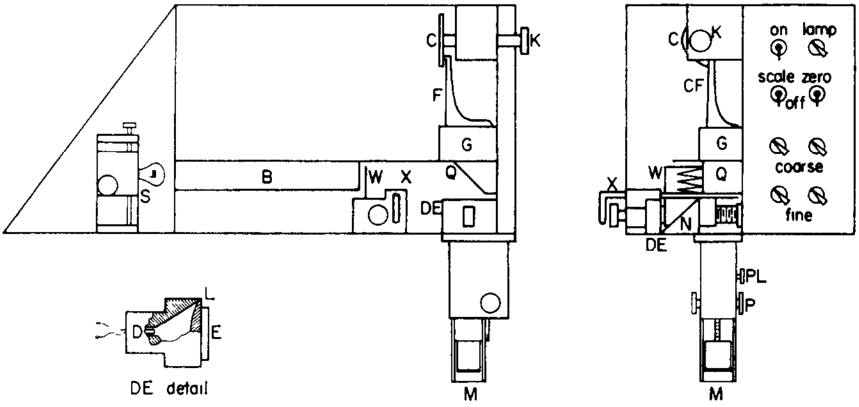

FIG. 2.—Left portion: side view of the instrument with panel removed. Right portion. front view of instrument with left half of front panel removed
Inset: details of the detector assembly block.
DE, detector assembly; *K*, wavelength knob; *PL*, path-length lock, other identification as in Fig. 1.

locking set-screw, *PL*, is provided. The range of the probe drive is about 5 cm, which allows continuous path-length adjustment from 0 to 10 cm. Longer path-lengths are achieved by extending the stage legs.

The wavelength is set with knob *K* which drives the cam and thereby rotates the grating. A wavelength scale viewed through a window in the non-hinged portion of the front panel is attached to the cam shaft. (Scale and front panel are not shown in Fig. 2.)

The circuit employed (shown schematically in Fig. 3) is similar to those used in previous designs.[1,6,7] It will be noted that the circuit is basically a series arrangement of photodetector, detector power supply, and output device. The particular circuit shown is designed for use with a Rubicon galvanometer. The model selected has a sensitivity of about 0·0006 μA/mm over the 100-mm scale, an internal resistance of about 4·5 kΩ, and a critical damping resistance of about 85 kΩ. In order to ensure linear response of the IN2175 the resistances of all components in series with the detector have been kept as low as possible.

The batteries shown in the circuit are mercury cells. Two 12-V batteries are used as the main source; 1·34-V cells are used in the control circuits.

The zero-shift circuit provides a simple method of adjusting the galvanometer to zero, thereby compensating for the dark current. Fine adjustment of this circuit involves changing the resistance of the cell circuit; however, this change has a negligible effect on the damping behaviour and sensitivity of the galvanometer and the sensitivity of the detector and the linearity of its response. Operation with the scale expanded to the right (beyond 100% transmittance) is readily made possible by appropriate adjustment of the light intensity. The scale-shift circuit provides the much needed additional capacity of expanding the scale to the left (below 0% transmittance). The circuit yields up to about 400 scale divisions of shift without affecting the linearity of response. The current drain in both circuits (zero shift and scale shift) is extremely small.

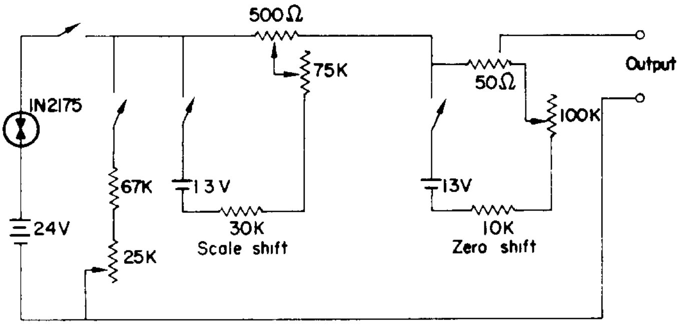

FIG. 3.—Schematic diagram of the detector and shift circuits

The exciter lamp is actuated by a step switch which permits selection of either 2, 4, or 6 V operation, and thereby coarse adjustment of the light intensity. Fine adjustment is achieved by using the comb, *W*. The step voltages are provided by two 6-V lead storage batteries connected in parallel and tapped at individual cells. Two batteries are required, since at 6 V the lamp runs at a current of about 1·25 A.

Performance tests

A tuning procedure is used to calibrate the grating. An interference filter is placed in the optical path, the knob *K* is set at the wavelength of the filter, and the cam follower is adjusted for maximum detector output. No resetting of the cam follower was necessary when verifying the calibration at several additional wavelengths, thus indicating proportionality between the linear scale and the wavelength.

The linearity of response and the stability of the entire instrument were tested by the methods previously described.[1] Linearity up to an absorbance of about 0 8 was demonstrated. No short term fluctuations were noted, and long term drift did not exceed 0 2 scale divisions/hr. Linearity was also confirmed when the instrument was used with recorder output.

The effectiveness of exclusion of ambient light was demonstrated by illuminating the probe assembly with a 100-W tungsten bulb. No deviations in instrument reading could be detected.

APPLICATION

The utility of the full-immersion design for a *phototitrator* has been demonstrated by routine use in the authors' laboratory. The instrument has satisfied the design criteria of simplicity, ease of operation, versatility, ruggedness, stability, and low cost. Photometric titrations have been conducted both manually and automatically. For the latter purpose a Sargent Recorder and a constant flow burette were used.

Although the original intention was to construct a phototitrator, the instrument described here can equally well be used as a *photometer*, which shows the advantages of freedom from restrictions on ambient light conditions and cell configuration. In fact the photometer functions with the ruggedness and simplicity normally associated with a modern pH meter, and is used in much the same manner. The probe is first immersed in a reference solution for "calibration" of the scale, then after brief rinsing, the probe is dipped in the test solution. Any beaker or other vessel large enough to accommodate the light probe can be used.

Exactly reproducible adjustment of a certain path-length is difficult with the variable path-length probe, although not impossible if a pair of calipers is used. However, for analytical purposes such an adjustment is seldom required. Normally, a determination is made within the rectilinear portion of the calibration curve, *i.e.*, in the range where Beer's law is obeyed. Then, all that is needed is an approximate reproduction of the path-length and one calibrating measurement on a standard solution. Thus, the variable path-length probe can be used in photometric determination although with limitation. However, it is not difficult to construct probe assemblies with fixed and precise light-paths. Several such designs have been built and tested. The following one proved to be most convenient. A glass tube is closed at its lower end by a glass plate. Sections of the tube extend below the window to support a mirror. The spacing between the mirror surface and the window is set at exactly half the desired path-length. The upper end of the tube is mounted in a brass cylinder which is secured to the body of the instrument by a bayonet fitting, thus allowing ready interchange of probes of different path-lengths.

The full-immersion instrument, in a special application, gave a very simple solution to an aggravating problem. Time studies of reactions in deeply cooled solutions were needed in a particular investigation. To perform such photometric studies with a common photometer is quite difficult because special arrangements are necessary to avoid fogging of the cuvette containing the cold liquid. Even with appropriate aspiration of dry air along the cuvette, difficulties exist because the relatively small amount of solution in the cuvette possesses insufficient heat capacity to maintain the low temperature. With the light tube of the immersion photometer sealed also at its upper end (after filling with a dry gas) by glueing on a thin plate of glass, no fogging occurs. Maintaining the desired low temperature was no longer a problem because the vessel containing the test solution could simply be immersed in a cooling solution.

It should finally be pointed out, however, that beyond a few tests and the application just described, the value of the instrument and its accuracy and precision as a spectrophotometer have not yet been fully assessed.

Operation

One special feature of this design is the capacity for scale expansion by zero suppression (that is, scale shift to the left). Since this feature can be employed in either of the two uses of the instrument, the procedure of programming a 100-division shift will be described first.

Programming for zero suppression Select any wavelength, attach any probe assembly and set zero with the scale-shift circuit off. To set zero, close shutter *X*, activate the zero-shift circuit and operate its controls to bring the pointer exactly to the zero mark. Next set 100% transmittance as follows. Open the shutter *X*, and select (by turning the step switch) a lamp voltage that gives the minimum light intensity for at least full-scale deflection. Then bring the pointer exactly to the 100 mark by operating the comb, *W*. Now activate the scale-shift circuit and operate its controls to bring the pointer from the 100 mark back exactly to the zero mark. The instrument is now programmed. In any later operation (provided, of course, the respective controls remain untouched) if the scale shift circuit is activated, the pointer will be shifted 100 scale divisions to the left.

With the instrument programmed as described the effective zero is at −100 scale divisions. The pointer may now be moved back to the 100 mark by operating the lamp step-switch or the comb or both. The range between zero and 100% transmittance is then 200 scale divisions, of which, however, only the upper half is displayed. If, during the later operation of the instrument, the pointer moves below the zero mark, deactivation of the scale-shift circuit displays the lower half of the 200 scale division range.

Zero suppression for 200 and more scale divisions (up to a total of 400) is possible. However, suppression by 100 scale divisions was found sufficient for all present purposes of the instrument and no attempt was made to incorporate the necessarily more complicated circuit for higher suppressions.

Photometer operation. First set the desired wavelength and path-length. The latter may be accomplished either by attaching the appropriate fixed-path-length probe or by attaching the variable-probe assembly and adjusting it to the required path-length. Set zero as described above. Set 100% transmittance as described above but with the probe immersed in the reference solution. Remove the vessel containing the reference solution, immerse the probe in the sample solution and read % transmittance. Zero suppression may be employed as needed.

Titrator operation. Two principle cases may be differentiated. A down-scale titration in which the pointer moves left (that is, to lower transmittance values) as the titration proceeds, and an up-scale titration in which the opposite takes place.

(*i*) *Down-scale titrations.* Select the desired wavelength, set zero and attach the variable probe assembly with the appropriate path-length adjusted. Immerse the probe in the sample solution and bring the pointer to the 100-mark by operating the lamp step-switch or the comb or both. Start adding titrant and take readings after addition of each increment and plot the results. Selection of the optimum path-length may be difficult if not known from prior experience with a particular titration system. In such an event a test titration with an aliquot of the sample solution may be performed. The probe is immersed, the pointer brought near the 100-mark and excess of titrant is added. Thus, the range of pointer movement is readily established. If only a limited amount of sample solution is available, the titration may be performed with about half of the sample solution, the path-length adjusted accordingly, and then the rest of the solution added and the titration finished.

Increased sensitivity may be secured by utilizing the zero suppression as described above.

(*ii*) *Up-scale titration.* This type of titration is somewhat more difficult because it requires specific knowledge of the position of the pointer at or past the end-point. It is, of course, possible to operate in the following way. Set zero as usual and 100% transmittance with the solvent as the reference. Then the pointer will definitely stay on scale during the titration but the capability of the instrument to yield highest sensitivity is not utilized It is better to adjust the 100-mark with an over-titrated solution. When doing so, the lamp step-switch, comb and above all the variability of the path-length should be employed in conjunction, to achieve the optimum range of pointer movement. It should be noted that actually the adjustment is not made to the 100-mark but rather to 95 or even 90 scale divisions in order to allow for the increase in transmittance due to dilution effects during the titration. Alternatively, adjustment to the 100-mark may be made if the pointer passes beyond that mark the scale shift circuit (correctly programmed for 100 scale divisions) may be activated to bring the pointer back on scale.

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Zusammenfassung—Eine Anordnung zur photometrischen Titration wird beschrieben, die Einrichtungen zur Veranderung der Schichtdicke Nullpunktsunterdruckung und Skalendehnung einschließt. Das Instrument kann auch als einfaches Spektrophotometer verwendet werden

Résumé—On décrit une étude pour un appareil de titrage photométrique qui comprend des facilités pour une longueur de marche variable, la suppression du zéro et l'extension de l'échelle. On peut aussi utiliser l'instrument comme un spectrophotomètre simple.

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SHORT COMMUNICATIONS

Determination of ultramicro amounts of selenium by gas chromatography

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o-PHENYLENEDIAMINE reacts quantitatively with selenous acid to form piaselenol, which can be extracted into toluene [1] 5-Chloropiaselenol is similarly formed and a toluene solution of it is very sensitive to electron-capture detection in gas chromatography. Ultramicro amounts of selenium, which are converted into 5-chloropiaselenol by 4-chloro-*o*-phenylenediamine in acidic solution, can be extracted into 1 ml of toluene and determined with a gas chromatograph equipped with an electron-capture detector.

EXPERIMENTAL

Reagents

4-Chloro-*o*-phenylenediamine hydrochloride was purified by a method previously described.[2] A 0·5% aqueous solution was prepared just before use. A stock selenium solution (80 μg/ml) was prepared by dissolving 56·2 mg of selenium dioxide in 500 ml of water. Solutions containing from 0·08 to 0·80 μg of selenium were prepared from it by dilution.

5-Chloropiaselenol was prepared as described previously [3] Hydrochloric acid, toluene and other reagents were of analytical reagent grade.

Apparatus

A Shimadzu Model GC-3AE gas chromatograph (Kyoto, Japan) equipped with an electron-capture detector was used. The glass column (2 m long, 4 mm bore) was packed with 15% SE-30 on 60–80 mesh Chromosorb W.

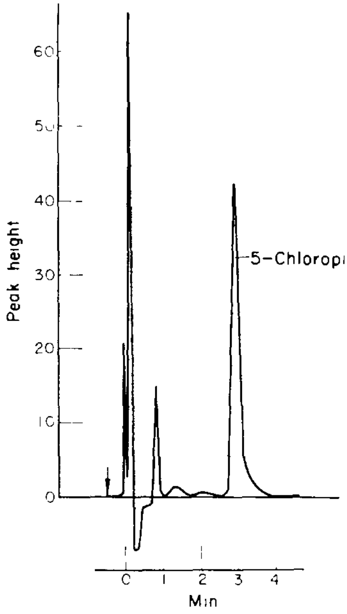

FIG. 1.—Gas chromatogram of 5-chloropiaselenol extracted (0·40 μg Se in 1 ml of toluene). Sensitivity 10^2 MΩ, Range 0·2 V.

The column and detector temperature was maintained at 200°C. The nitrogen flow-rate was 50 ml/min A Shimadzu Model 250A recorder was used and the chart speed was 10 mm/min.

Sensitivity of piaselenol derivatives to electron-capture detection

5-Chloro- and 4,5-dichloropiaselenol have a high sensitivity to electron-capture detection, the latter being three times more sensitive than the former. However, 4-chloro-*o*-phenylenediamine was used to determine selenium, because 4,5-dichloro-*o*-phenylenediamine was not commercially obtainable. However, 5-chloropiaselenol has adequate sensitivity and its extractability into toluene from acidic solution is greater than that of piaselenol.[4]

The gas chromatogram of 5-chloropiaselenol is shown in Fig. 1

Calibration curve

Portions of selenous acid solution containing from 0·08 to 0·8 μg of selenium are put into 100-ml separatory funnels and diluted to about 40 ml with distilled water; the pH is adjusted to between 0 and 1 with hydrochloric acid. Then 2 ml of 0·5% 4-chloro-*o*-phenylenediamine solution are added to each and the solutions are allowed to stand for 2 hr. The 5-chloropiaselenol is extracted into 1 ml of toluene by shaking for 5 min. The layers are separated and 5 μl of the toluene extract are injected into the gas chromatograph and the recorded peak-height is measured The calibration curve is linear up to 0·80 μg of selenium.

As the sensitivity of an electron-capture detector tends to vary during operation, a series of experiments should be carried out successively and an unknown content of selenium should be determined along with standard samples which contain similar amounts of selenium.

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Summary—4-Chloro-*o*-phenylenediamine reacts with selenous acid at pH 0–1 to form 5-chloropiaselenol, which is then extracted into 1 ml of toluene. The toluene layer is injected into an electron-capture detector gas chromatograph. From the peak height selenium is determined, the minimum amount detectable being about 0·04 μg.

Zusammenfassung—4-Chlor-o-phenylendiamin reagiert mit seleniger Sáure bei pH 0–1 zu 5-Chlorpiaselenol, das in 1 ml Toluol extrahiert wird. Die Toluolschicht wird in einen Gaschromatographen mit Elektroneneinfangdetektor injiziert. Selen wird aus der Peakhohe bestimmt, die kleinste nachweisbare Menge ist etwa 0,04/ug.

Résumé—La 4-chloro *o*-phénylènediamine réagit avec l'acide sélénieux à pH 0–1 pour former le 5-chloropiasélénol, que l'on extrait dans 1 ml de toluène La couche toluénique est injectée dans un chromatographe en phase vapeur avec détecteur à capteru d'électron. De la hauteur du pic, on détermine le sélénium, la quantité minimale décelable étant d'environ 0,04 μg

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Zusammenfassung—Verfahren zur Bestimmung von Cyanid (10^{-8}–$10^{-5}M$) und Sulfid (10^{-7}–$10^{-5}M$) werden beschrieben, die daruf beruhen, daß diese Ionen die Inhibition von Invertase durch Quecksilber(II) oder Silber aufheben. Jod (0,1–3 µg) laßt sich durch seine Inhibitionswirkung auf Invertase bestimmen.

Résumé—On décrit des méthodes pour le dosage du cyanure (10^{-8}–$10^{-5}M$) et du sulfure (10^{-5}–$10^{-7}M$) basées sur l'influence désinhibitrice de ces ions sur l'invertase inhibée par le mercure(II) ou par l'argent. L'iode (0,1–3 µg) peut être déterminé par son inhibition de l'invertase.

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Spectrophotometric determination of tartrate in the presence of citrate

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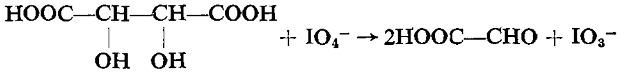
RECENTLY a method was developed for the spectrophotometric determination of µg-amounts of *vic*-dihydroxy compounds[1] based on rapid oxidation of the compound with periodate, followed by spectrophotometric determination of the iodate as tri-iodide after reaction with iodide. The excess of periodate is masked with molybdate at pH 3.[2] As this reaction had already been applied to the detection of 0.1 µg of tartrate,[3] it was decided to apply the spectrophotometric procedure to the determination of traces of tartrate, especially in the presence of citrate.

There is a dearth of reliable methods for the determination of small amounts of tartrate, especially in the presence of citrate,[4] and there is also a remarkable lack of knowledge about the chemical reactions occurring in those procedures that are most widely used. The most widely used spectrophotometric method is based on the formation of a red colour when a solution of metavanadate is acidified with acetic acid in the presence of tartrate[5] enabling as little as 20 µg of tartrate to be determined[6] without interference from citrate. The colour is, however, unstable in daylight, the intensity reaching a maximum after 10 min,[5] and then fading, so that measurements have to be made after a definite time interval,[5–7] or the colour must be allowed to develop in the dark, in which it is stable.[8,9] The reaction of tartrate with Fenton's reagent to give a lavender colour has also been used as the basis of a spectrophotometric method for tartrate,[10] but the reaction conditions must be accurately reproduced for successful determinations. Addition of iron(II) to a tartrate solution, followed by dinitrophenylhydrazine and hydroxide, produces a purple colour, which has been used for the spectrophotometric determination of 7–50 µg of tartrate,[11] citrate, malate and α-keto-acids interfere. Condensation with *p*-dimethylaminobenzaldehyde has likewise been applied to the determination of 20–100 µg of tartrate,[6] and formation of the 2,4-dinitrophenylhydrazone of glyoxylic acid formed by reaction of tartrate and periodate, to determination of 3–45 µg of tartrate.[12]

The most sensitive method reported[13] involves the chromatographic separation of tartrate (2–30 µg) on paper impregnated with nickel hydroxide. The nickel tartrate spot is revealed with dithio-oxamide and the tartrate is determined by cutting out the spot and weighing it. The reproducibility is claimed to be ±1.6%. Larger amounts of tartrate have been determined polarimetrically[14,15] and titrimetrically after reaction with periodate[16,17] or lead tetra-acetate.[16]

Determination of tartrate

Tartaric acid is oxidized by periodate in two consecutive reactions which can be represented as:



$$\underset{\mathrm{OH}\quad\;\mathrm{OH}}{\mathrm{HOOC{-}CH{-}CH{-}COOH}} + \mathrm{IO_4^-} \rightarrow \mathrm{2HOOC{-}CHO} + \mathrm{IO_3^-} \qquad (1)$$

$$\mathrm{HOOC{-}CHO} + \mathrm{IO_4^-} \rightarrow \mathrm{CO_2} + \mathrm{HCOOH} + \mathrm{IO_3^-} \qquad (2)$$

Reaction (1) is much more rapid[18] than reaction (2). For the most sensitive determination of tartrate, it would be desirable for complete oxidation to carbon dioxide and formic acid to occur, so that 3 moles of iodate are produced per mole of tartrate oxidized. The procedure previously developed for aldohexoses[1]—by oxidation at 45–50° in the presence of a large excess of periodate—but omitting the use of sulphuric acid, gives quantitative oxidation of 30 μg of tartrate to carbon dioxide and formic acid within an hour. No further oxidation occurs at this temperature, although some, perhaps of the formic acid, may occur when the oxidation is carried out at 70–80°. This procedure was applied to the analysis of pure solutions of ammonium tartrate. The results are given in Table I.

TABLE I.—DETERMINATION OF TARTRATE (CONSUMING 3 MOLES OF IO_4^-)

Taken, μg	5·0	7·5	10·0	15·0	20·0	22·5	30·0
Found,* μg	5·2	7·8	10·0	15·2	20·3	23·4	30·2
No. of determinations	3	2	3	5	3	2	2

* Mean

Determination of tartrate in the presence of citrate

Under normal reaction conditions, citrate is not oxidized by periodate, and only very large concentrations of citrate interfere in the qualitative test for tartrate[8] based on the same reactions as the spectrophotometric procedure described above. The determination of tartrate in the presence of moderately large amounts of citrate by this procedure seemed a possibility, but under the reaction conditions required for complete oxidation of tartrate, mg-amounts of citrate reacted appreciably and unceasingly for at least 2·5 hr. Table II compares the behaviour of various amounts of tartrate and citrate in this procedure. The continuance of the oxidation beyond the time required for tartrate oxidation shows that the effect is not mainly due to tartrate impurity in the citrate. Indeed, a comparison of the initial rates of production of iodate by tartrate and citrate indicates that the tartrate impurity in the citrate must be significantly less than 1%.

TABLE II.—COMPARISON OF IODATE PRODUCTION BY TARTRATE AND CITRATE

	Absorbance after					Reaction conditions
	0·5 hr	1·0 hr	1·5 hr	2·0 hr	2·5 hr	
Tartrate ($2 \times 10^{-6} M$)	0·46	0·48			0·46	at 50°, with $4 \times 10^{-4} M\ IO_4^-$
Citrate ($2 \times 10^{-4} M$)	0·30	0·45			1·90	
Tartrate ($6·7 \times 10^{-7} M$)	0·12	0·16		0·16		at 50°, with $10^{-4} M\ IO_4^-$
Citrate ($10^{-5} M$)	0·05	0·13	0·17	0·35		
Citrate ($8 \times 10^{-3} M$, 38 mg)	0·07	0·08	0·09		0·10	at 0°, with $4 \times 10^{-5} M\ IO_4^-$

As the reaction conditions were too vigorous, milder conditions were tried under which tartrate would be oxidized only to glyoxylic acid and citric acid would not be oxidized at all. At 0° the reaction conditions previously used for mannitol and sorbitol[1] gave complete oxidation of tartrate (≤ 60 μg) to the aldehyde within 30 min with no measurable further oxidation for 15 min, after which further oxidation occurred very slowly, the absorbance increasing by *ca.* 6% in the next 15 min. Results for the analysis of pure solutions of ammonium tartrate by this less sensitive procedure are given in Table III. The behaviour of citrate (38 mg) in this procedure is included in Table II. Smaller amounts gave smaller blank absorbance values, almost independent of quantity of citrate, 1·9 mg, 0·015, 95 μg, 0·002.

TABLE III.—DETERMINATION OF TARTRATE (CONSUMING 1 MOLE OF IO_4^-)

Taken, μg	15·0	30·0	45·0	60·0	75·0
Found, μg	16·1	31·2	45·4	60·2	74·3

Very large amounts of citrate interfere in this procedure because the citrate then complexes an appreciable portion of the molybdate present, and thus demasks the excess of periodate. Experiments showed that demasking of a final solution $2 \times 10^{-2} M$ in molybdate and $4 \times 10^{-5} M$ in periodate becomes significant when the solution is also $>1·2 \times 10^{-2} M$ in citrate. However, it is desirable that the citrate should be $<1·2 \times 10^{-3} M$ if the blank absorbance is to be $<0·03$. Citrate absorbs slightly at 350 nm, so the blank solution must contain a similar amount of citrate to the unknown sample. Results obtained for the determination of tartrate (15–60 μg) in the presence of citrate (38 mg) are given in Table IV.

TABLE IV.—DETERMINATION OF TARTRATE IN THE PRESENCE OF CITRATE (38 mg)

Taken, μg	15·0	30·0	45·0	60·0
Found, μg	16·0	32·1	47·2	60·0
	14·4	30·2	43·6	58·5
	16·2	30·2	45·2	59·7

The maximum amount of tartrate present in the citrate sample used was established by measuring the difference in absorbance between blank solutions in which the citrate was added to masked and unmasked periodate solutions respectively. Only in the latter solution would oxidation by periodate occur, whereas other contributions to the blank absorbance (absorbance of molybdate, periodate, citrate, and that arising from traces of iodate in the periodate) would be the same in both solutions. The mean absorbance given by 38 mg of citrate in this way was 0·03, which would correspond to a tartrate content of 3 μg. But this is likely to be too high because the slight oxidation of citrate itself must contribute to this value. Thus the citrate used in this investigation would be suitable as a source of tartrate-free citrate for incorporation in blank solutions.

EXPERIMENTAL

Absorbance measurements were made at 350 nm on a Beckman DB spectrophotometer, in 1-cm cells. Analytical-grade ammonium tartrate and laboratory reagent trisodium citrate were used. Stock solutions were as previously described.[1]

Determination of tartrate in the absence of citrate by oxidation with 3 moles of periodate

Add to a 50-ml graduated flask an aqueous tartrate solution (0·3–2·5 ml, containing 5–40 μg of tartrate). Add $10^{-2}M$ periodate solution (1 ml) and wash the stem of the flask with sufficient water to bring the volume to 2·5 or 5·0 ml. Heat on a water-bath at 45–50° for 1 hr. Cool, add molybdate solution (10 ml), buffer solution (5 ml) and iodide solution (10 ml). Allow to stand for 30 min, and measure the absorbance *vs.* a water blank taken through the whole procedure. Obtain the concentration of iodate formed from the calibration curve prepared by using aliquots of a standard iodate solution.[1] The concentration of tartrate is one-third of the iodate concentration.

Determination of tartrate in the presence of citrate

Add to a 50-ml graduated flask, $\not>$6 mg of citrate containing tartrate as an impurity. Dissolve it in 3 ml of water, add $10^{-3}M$ periodate solution (2 ml), and allow to stand in ice for 30–40 min. Add molybdate solution (10 ml), buffer solution (1 ml) and iodide solution (5 ml). Allow to stand for 30 min, and measure the absorbance *vs.* a blank of the same quantity of tartrate-free citrate taken through the whole procedure. The tartrate concentration is the same as that of the iodate formed, as read from the calibration graph.

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Summary—Methods are described for the determination of 5–30 μg of tartrate alone and of 15–60 μg in the presence of up to 6 mg of citrate, based on oxidation by 3 moles or 1 mole of periodate respectively. The iodate formed is determined spectrophotometrically at 350 nm as tri-iodide after reaction with iodide, the excess of periodate being masked with molybdate.

Zusammenfassung—Methoden zur Bestimmung von 5–30 μg Tartrat allein und von 15–60 μg in Gegenwart von bis zu 6 mg Citrat werden beschrieben, die auf der Oxidation mit 3 Mol bzw. 1 Mol Perjodat beruhen. Das gebildete Jodat wird nach Reaktion mit Jodid spektrophotometrisch bei 350 nm als Trijodid bestimmt, wobei der Perjodatüberschuß mit Molybdat maskiert wird.

Résumé—On décrit des méthodes pour le dosage de 5–30 μg de tartrate seul et de 15–60 μg en la présence de citrate jusqu'à 6 mg, basées sur l'oxydation par 3 moles ou 1 mole de periodate respectivement. On dose l'iodate formé spectrophotométriquement à 350 nm à l'état de triiodure après réaction avec l'iodure, l'excès de periodate étant dissimulé au moyen de molybdate.

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Determination of metallic iron, iron(II) oxide, and iron(III) oxide in a mixture

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AVAILABLE literature records various methods for the determination of metallic iron in presence of iron(II) and iron(III) oxides,[1,2] but gives less information on a rapid, accurate, and dependable method for the determination of all the three together. Metallic iron has been determined *via* reduction of a copper(II) salt[3] or mercury(II) chloride[4] in aqueous medium followed by permanganate titration. Copper sulphate has also been suggested for the determination of metallic iron, but errors arise from the formation of soluble copper(I) salts [1,5] Habashy[6] suggested the use of mercury as a catalyst in the copper sulphate method. According to Weiss,[7] use of larger quantities of mercury(II) chloride to dissolve iron would favour the formation of calomel, but the latter tends to occlude some of the iron, causing low results. Morris[8] pointed out that recoveries of iron are incomplete with samples coarser than 65-mesh Aubry and Perrot[9] prefer alcoholic mercury(II) chloride solution and determine iron in the filtrate by first oxidizing it with persulphate and then titrating with titanium(III). Wakamatsu[10] titrated the iron(III) in the filtrate with standard EDTA solution at 40° with Tiron as indicator; mercury(II) did not interfere. When the oxides are also to be determined, the residue after the mercury(II) chloride reaction has to be treated first to remove mercury(I) chloride and/or mercury. Aubry and Perrot[9] suggest the use of alcoholic iodine solution for this purpose, whereas Stognii[11] heats the dried precipitate in a stream of chlorine at 200–22° for an hour. Other methods for the determination of metallic iron include oxidation with iron(III),[12–14] displacement of silver by iron in $Ag(NH_3)_4(SCN)_4$,[15,16] measurement of hydrogen evolved by reaction with an acid,[17,18] conversion into iron(II) sulphide by fusion with sulphur, followed by determination of the hydrogen sulphide,[19] reduction of lead chloride solution,[20] and reaction with bromine in ethanol [21] Except the last, these methods either do not permit subsequent determination of iron oxides or are too lengthy and involved for precise routine analysis The bromine method[21] depends on the selective dissolution

Résumé—On décrit des méthodes pour le dosage de 5–30 μg de tartrate seul et de 15–60 μg en la présence de citrate jusqu'à 6 mg, basées sur l'oxydation par 3 moles ou 1 mole de periodate respectivement. On dose l'iodate formé spectrophotométriquement à 350 nm à l'état de triiodure après réaction avec l'iodure, l'excès de periodate étant dissimulé au moyen de molybdate.

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Determination of metallic iron, iron(II) oxide, and iron(III) oxide in a mixture

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AVAILABLE literature records various methods for the determination of metallic iron in presence of iron(II) and iron(III) oxides,[1,2] but gives less information on a rapid, accurate, and dependable method for the determination of all the three together. Metallic iron has been determined *via* reduction of a copper(II) salt[3] or mercury(II) chloride[4] in aqueous medium followed by permanganate titration. Copper sulphate has also been suggested for the determination of metallic iron, but errors arise from the formation of soluble copper(I) salts [1,5] Habashy[6] suggested the use of mercury as a catalyst in the copper sulphate method. According to Weiss,[7] use of larger quantities of mercury(II) chloride to dissolve iron would favour the formation of calomel, but the latter tends to occlude some of the iron, causing low results. Morris[8] pointed out that recoveries of iron are incomplete with samples coarser than 65-mesh Aubry and Perrot[9] prefer alcoholic mercury(II) chloride solution and determine iron in the filtrate by first oxidizing it with persulphate and then titrating with titanium(III). Wakamatsu[10] titrated the iron(III) in the filtrate with standard EDTA solution at 40° with Tiron as indicator; mercury(II) did not interfere. When the oxides are also to be determined, the residue after the mercury(II) chloride reaction has to be treated first to remove mercury(I) chloride and/or mercury. Aubry and Perrot[9] suggest the use of alcoholic iodine solution for this purpose, whereas Stognii[11] heats the dried precipitate in a stream of chlorine at 200–22° for an hour. Other methods for the determination of metallic iron include oxidation with iron(III),[12–14] displacement of silver by iron in $Ag(NH_3)_4(SCN)_4$,[15,16] measurement of hydrogen evolved by reaction with an acid,[17,18] conversion into iron(II) sulphide by fusion with sulphur, followed by determination of the hydrogen sulphide,[19] reduction of lead chloride solution,[20] and reaction with bromine in ethanol [21] Except the last, these methods either do not permit subsequent determination of iron oxides or are too lengthy and involved for precise routine analysis The bromine method[21] depends on the selective dissolution of metallic iron. The oxide residue is analysed for iron(II) and iron(III) by the usual methods. The principal advantage of this approach is that the oxides are not contaminated by reaction products from the iron dissolution.

The present paper records a simple and reasonably accurate procedure for the determination of metallic iron and iron(II) and (III) oxides

EXPERIMENTAL

Reagents

Iron powder and magnetite were prepared from reagent-grade iron(III) ammonium sulphate. Hydrous iron(III) oxide was precipitated, washed, dried and ignited to iron(III) oxides, which was reduced to metallic iron with dry hydrogen or to magnetite with moist hydrogen. Details will be published elsewhere. Synthetic mixtures containing known amounts of metallic iron and iron(II) and (III) oxides were prepared from the pure iron powder and magnetite.

All chemicals used were of analytical reagent quality.

Apparatus

The reaction vessel was a 500-ml glass-stoppered conical flask with a B24 joint The stopper was made with an inlet and an outlet for carbon dioxide, and had a central capillary tube ending in a porosity-3 sintered-glass disc; the capillary was coaxial with the inlet tube and the sintered disc was about 1 mm above the base of the flask. The capillary was connected to another 500-ml flask connected to a water pump through a trap.

Procedure

Transfer an accurately weighed sample (*ca.* 200 mg) into the 500-ml reaction flask without its stopper. Add 100 ml of freshly prepared 2% bromine solution in ethanol and stir magnetically for 60–90 min to dissolve the metallic iron. Put the stopper in place, connect the second flask and the trap, and start the filter pump. Wash the residue first with ethanol and then with water. Disconnect the second flask which contains the filtrate and the washings. Add ammonium hydroxide to precipitate the iron(III) and then reprecipitate it. Filter off the precipitate, wash it with 2% ammonium chloride solution, dissolve it in hydrochloric acid(1 + 1), add potassium iodide and titrate with 0·1*N* sodium thiosulphate

Connect the flask containing the oxide residue to a carbon dioxide generator. Dissolve the oxides in hydrochloric acid in an inert atmosphere, heating if necessary. Cool, adjust the acidity to 4–5*N*, and titrate the iron(II) with 0·1*N* sodium vanadate, using 10 drops of 0·2% *N*-phenylanthranilic acid indicator. Dilute the titrated solution to bring the acidity to 2*N*, and add a small quantity of sodium bicarbonate and an excess of potassium iodide. After 5 min, titrate the liberated iodine with 0·1*N* sodium thiosulphate. The first titration gives the iron(II) oxide, and the difference of the two titrations gives the iron(III) oxide.

RESULTS AND DISCUSSION

Typical results are given in Table I. Preliminary experiments showed that the bromine solution did not affect the iron(II) and (III) oxides

TABLE I —DETERMINATION OF Fe, FeO, AND Fe_2O_3 IN A MIXTURE

Fe, %		FeO, %		Fe_2O_3, %	
Calculated	Found	Calculated	Found	Calculated	Found
15·4	15·2	19·5	19·6	64·2	65·1
19·4	19·6	18·6	18·9	61·1	61·7
28·8	28·3	16·5	16·7	54·0	53·7
29·1	28·6	16·4	17·0	53·7	52·8
34·6	34·2	15·2	15·7	49·5	49·7
43·6	43·5	13·2	13·0	42·6	41·6
47·4	46·5	12·3	12·8	39·6	40·7
57·0	57·3	10·1	9·8	32·4	32·5
63·0	62·9	8·8	9·0	27·8	27·6

Von Vogel[21] reduced iron(III) and titrated with permanganate (Zimmermann–Reinhardt procedure), but we found it more convenient to use iodometric titration, the main advantage being avoidance of the reduction step.

Generally, iron(II) and (III) oxides are determined by dissolution in hydrochloric acid in a carbon dioxide atmosphere, followed by titration of iron(II), and determination of total oxide on a separate sample. In the procedure described here only one sample is required for the entire analysis If desired dichromate can be used instead of vanadate as titrant, but the ethanol must then be removed completely after the bromine reaction. Vanadate is preferred as the ethanol does not interfere. *N*-phenylanthranilic acid is used as indicator to avoid addition of phosphoric acid, which would interfere with the iodometric titration.

In the first experiments, the oxides of iron after the bromine reaction were filtered off on a sintered-glass crucible, but it was found difficult in the dissolution step, to remove all the oxides from the filter. In the apparatus described here, the residue remains in the original flask; this system was found extremely convenient even when an inert atmosphere was to be maintained.

The results for metallic iron are satisfactory but the errors in the determination of the oxides are rather higher than those normally expected in quantitative analysis. However, the results are considered satisfactory in view of the nature of the mixture and the simplicity and rapidity of the determination.

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Summary—A procedure is described for the estimation of metallic iron, ferrous oxide, and ferric oxide when present together. The sample is treated with bromine dissolved in ethanol, and filtered. Iron in the filtrate is titrated iodometrically, and corresponds to the metallic iron present in the mixture. The oxide residue is dissolved in hydrochloric acid under a carbon dioxide atmosphere. The iron(II) formed, equivalent to FeO present, is titrated with a standard vanadate solution, and the total iron(III) ($\equiv$FeO + Fe_2O_3) in the titrated solution is then estimated iodometrically.

Zusammenfassung—Ein Verfahren zur Bestimmung von metallischem Eisen, Eisen(II)- und Eisen(III)oxid nebeneinander wird beschrieben Die Probe wird mit einer athanolischen Bromlosung behandelt und filtriert Das Eisen im Filtrat wird jodometrisch titriert und entspricht dem vorhandenen metallischen Eisen. Der Oxidruckstand wird unter Kohlendioxid in Salzsaure gelost. Das gebildete Eisen(II), das dem vorhandenen FeO entspricht, wird mit eingestellter Vanadatlosung titriert und dann das gesamte Eisen(III) (entsprechend FeO + Fe_2O_3) in der austitrierten Losung jodometrisch bestimmt.

Résumé—On décrit une technique pour l'estimation du fer métallique, de l'oxyde ferreux et de l'oxyde ferrique lorsqu'ils sont présents ensemble. On traite l'échantillon au brome dissous en éthanol et filtre. Le fer du filtrat est titré iodométriquement, et correspond au fer métallique présent dans le mélange. On dissout le résidu d'oxydes en acide chlorhydrique sous atmosphère de gaz carbonique. Le fer(II) formé, équivalant au FeO présent, est titré par une solution étalon de vanadate et le fer(III) total (FeO + Fe_2O_3) dans la solution titrée est alors estimé iodométriquement.

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Separation of rhenium, tungsten and molybdenum by thin-layer chromatography

(*Received* 6 *May* 1968, *Accepted* 27 *May* 1968)

THERE is little information available on the separation of rhenium, tungsten and molybdenum by thin-layer chromatography (TLC), although alloys of these elements have become technologically important.[1] R_f values for rhenium, tungsten and molybdenum have been recorded for systems of reversed-phase TLC with TBP[2] and liquid-anion exchangers,[3] both in hydrochloric acid media, but no separations of the three elements were accomplished in these systems.

The present communication reports the evaluation of a number of solvent systems for resolution of the three elements on glass plates coated with silica gel. The best separation was obtained with methanol–3*M* hydrochloric acid (7:3) and methanol–1*M* ammonium nitrate–3*M* ammonia (14:5:1).

EXPERIMENTAL

A commercial silica gel(Wako-Gel, B—O) was slurried with 10% starch solution (3–4 ml per g of gel), and spread 250 μm thick on 25 × 100 mm² glass plates with an applicator. The plates were air-dried, activated for 30 min at 110° in an oven and finally stored in a desiccator over silica gel.

The thin layer was spotted 15 mm from one end with one or two dabs (2–4 μl) of the test solution from a glass capillary, and dried under a heat lamp The plate was placed in a glass tank, 120 mm high and 50 mm in diameter, and allowed to stand for 30 min to equilibrate with the tank atmosphere. Ascending development was carried out with the solvent systems listed in Table I, at a constant temperature of 25° until the solvent front had risen 65 mm This usually took 30–50 min. After development the plate was dried and the positions of the elements were located by spraying first with freshly prepared 0 1–0 2% toluene-3,4-dithiol solution in 0·25*M* sodium hydroxide and subsequently with conc hydrochloric acid. Rhenium(VII), tungsten(VI) and molybdenum(VI) showed as yellowish green, blue and green spots, respectively. Drying under a heat lamp enhanced the intensity.

DISCUSSION

In all the solvent systems examined the mobilities were in the order Re > Mo > W. The low R_f values for tungsten(VI) may be explained as due to the formation of insoluble hydrated tungstic acid. Increasing the methanol concentration above 70% v/v usually resulted in marked streaking of molybdenum(VI).

Except for the acetic acid, formic acid, and sodium acetate systems, the differences in R_f value were large enough to permit separation of the three elements. Increase of the acid concentration beyond 6*M* in the 7·3 methanol–hydrochloric acid system gave poorer resolution of rhenium(VII) and molybdenum(VI) When a mixture of the three elements is chromatographed the R_f values are usually a little lower than those obtained individually.

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Except for the acetic acid, formic acid, and sodium acetate systems, the differences in R_f value were large enough to permit separation of the three elements. Increase of the acid concentration beyond 6*M* in the 7·3 methanol–hydrochloric acid system gave poorer resolution of rhenium(VII) and molybdenum(VI) When a mixture of the three elements is chromatographed the R_f values are usually a little lower than those obtained individually.

TABLE I —R_f VALUES OF Re(VII), Mo(VI) AND W(VI) IN VARIOUS SOLVENT SYSTEMS

Solvent system (v/v)	Re	$R_f \times 100$ Mo	W
Methanol-1M HNO_3(7:3)	55	20	1·5
Methanol-5M HNO_3(7:3)	66	40	4·6
Methanol-8M HNO_3(7:3)	81	49	4·6
	64*	42*†	2·3*
Methanol-8M HNO_3(6:4)	59*	32*	1·5*
Methanol-10M HNO_3(7:3)	85	48	2·3
	71*	45*†	1·5*
Methanol-1M HCl(7:3)	64	31	2·3
Methanol-1M HCl(6:4)	68	27	3·1
Methanol-3M HCl(7:3)	86	46	3·8
	68*	44*	3·8*
Methanol-3·5M H_2SO_4(8:2)	85	57	8·5
	76*	42*†	6·2*
Methanol-3·5M H_2SO_4(7:3)	86	62	10
Methanol-3M $HClO_4$(7:3)	75	52	3·1
Methanol-5·7M HBr(7:3)	82	65	—
	78*	57*†	5·4*
Methanol-8·6M HBr(7:3)	85	62	1·5
Methanol-17M CH_3COOH(7:3)	23	0	0
Methanol-5·8M CH_3COOH(7:3)	52	0	0
Methanol-8·8M HCOOH(7:3)	42	0	0
Methanol-0·2M NH_4NO_3(7:3)	62	12	0
Methanol-1M NH_4NO_3(7:3)	73	17†	0
Methanol-5M NH_4NO_3(7:3)	55	3·8	0
Methanol-1M CH_3COONa(9:1)	88	5	0
Methanol-1M CH_3COONa(7:3)	80	28†	6·2
Methanol-1M NH_4NO_3-3M NH_3(14:5:1)	82	58	15
	75*	41*	6·9*

* Obtained with mixture of Re, Mo, W.
† Tailing.

Molybdenum(VI) tails slightly when present in mixtures and chromatographed with certain solvent systems, probably on account of co-precipitation with tungstic acid, followed by gradual release from the precipitate through the movement of solvent, resulting in slower advance.

Rhenium(VII) can be separated from molybdenum(VI) and tungsten(VI) in concentration ratios of Re:Mo from 100:1 to 1:100 with methanol-5·8M acetic acid (7:3), and Re:W from 5:1 to 1:100 with methanol-1M ammonium nitrate-3M ammonia (14.5:1). Molybdenum(VI) and tungsten(VI) can be separated in ratios of Mo:W from 5:1 to 1:40 with methanol-3M hydrochloric acid (7:3).

A great advantage of methanolic acid or salt solution systems is that the spots remain small and great sensitivity of detection is obtained with dithiol as spray reagent. The sensitivities attainable are 2 μg for rhenium(VII), 1·5 μg for tungsten(VI) and 0·1 μg for molybdenum(VI).

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Summary—Re(VII), W(VI) and Mo(VI) can be separated by thin-layer chromatography on silica gel. The best results are obtained with methanol-3M HCl (7:3) and methanol-1M NH_4NO_3-3M NH_3 (14:5:1). Dithiol is used as detection reagent.

Zusammenfassung—Re(VII), W(VI) und Mo(VI) konnen durch Dunnschichtchromatographie an Silicagel getrennt werden. Die besten Ergebnisse erzielt man mit Methanol-3M HCl (7:3) und Methanol-1M NH_4NO_3-3M NH_3 (14·5:1). Dithiol wird als Nachweisreagens verwendet.

Résumé—On peut séparer Re(VII), W(VI) et Mo(VI) par chromatographie en couche mince sur gel de silice. Les meilleurs résultats sont obtenus avec méthanol–HCl 3*M* (7:3) et méthanol–NH_4NO_3 1 *M*–NH_3 3*M* (14:5:1). On utilise le dithiol comme agent de détection.

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Critical evaluation of spiking of low-grade ore samples in activation analysis for gold and uranium

(*Received* 30 *January* 1968. *Accepted* 15 *April* 1968)

DISAGREEMENT often exists in chemical assay values for both gold and uranium in low-grade ore samples analysed in different laboratories.[1,2] Apart from gold that might be fully retained by carbon,[3] the normal fire assay can extract about 97% of the gold, even in microgram quantities.[4] A need exists to find an alternative analytical method.

It has been shown[5] that methanol mixing of 30 g of 200-mesh ore powder yields satisfactorily homogeneous ore samples. Non-destructive neutron-activation analysis of gold in ore samples could be done for concentrations up to 20 ppm of gold in 1·5-g portions. In principle, activation analysis of low-grade samples spiked with gold and uranium should thus be possible if good mixing can be obtained over the concentration range previously investigated.

EXPERIMENTAL

Gold spiking

A standard solution containing 0·06398 mg of gold per ml was prepared. Three 25-g amounts of a West Rand Consolidated Mines composite residue sample (70% of 200-mesh, 0·118 dwt Au/ton, 0·0034% U_3O_8) were placed in separate agate mortars and 391·7, 780·8 and 1563·0 mg of the standard gold solution were added. These spiked samples were dried under infrared lamps, after which methanol was added and the mixing procedure carried out for at least 30 min.[1]

Uranium spiking

A standard solution containing 9·51 mg of uranium per ml was prepared. Four 25-g amounts of a South Roodepoort composite ore sample (70% of 200-mesh; 6·83 dwt Au/ton, 0·0023% U_3O_8) were placed in separate agate mortars, and 1·501, 2·998, 6·007 and 11·912 mg of uranium were added by means of the standard solution. These samples were then dried and mixed as described above.

Irradiation procedure

Four 1·5-g portions of each spiked gold mixture were placed in quartz tubes (5·5 × 0·8 cm diameter, 0·1 cm wall thickness).[6] Three reference samples were prepared which contained about 7 mg of gold (dried sample of a solution containing 6·397 mg of gold per ml). Owing to shortage of material, only three blank ore-samples were weighed out.

Each capsule, for irradiation of the gold samples in the hydraulic rabbit of the SAFARI 1 reactor (6⅔ MW) at Pelindaba, contained the four quartz tubes nearly filled with a spiked gold sample, one tube which contained an unspiked sample (in three cases only) and a tube containing a gold reference sample.

Similarly, for the uranium determination, each capsule contained four 1·5-g portions of a spiked sample, and a uranium reference sample. Only two unspiked samples were available.

Each capsule was irradiated for 10 min in a thermal neutron flux of $6{\cdot}3 \times 10^{13}$ n.cm^{-2} sec^{-1}.

Counting analysis

The gamma-photopeak analysis was done on a 5-cm^3 co-axial Ge(Li)-diode and associated electronic equipment (TC130 Tennelec Preamplifier, TC200 Tennelec Amplifier, RIDL Bias Amplifier,

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The gamma-photopeak analysis was done on a 5-cm^3 co-axial Ge(Li)-diode and associated electronic equipment (TC130 Tennelec Preamplifier, TC200 Tennelec Amplifier, RIDL Bias Amplifier, Intertechnique 400-channel Analyzer) A "cooling" time of 4 days was allowed before the 412-keV gamma-peak present in the decay of gold-198 was analysed for all the irradiated gold analysis samples. For an unspiked sample, about 3000 counts in the peak were accumulated in 20 min. For the spiked and reference samples, the number of counts in the peak was well above 10000

For uranium, a longer "cooling" time was allowed, as the activated manganese (^{56}Mn) in these samples caused too high a Compton background [5] After 7 days the 277-keV peak from decay of neptunium-239, the first daughter product of uranium-239, was analysed. The number of counts accumulated in the peak for an unspiked sample was about 7000 in 15 min, whereas for spiked and reference samples, the total counts ranged from 20000 to 100000. The peak-analysis method has been described elsewhere [5]

DISCUSSION

The total peak counting rates were corrected for differences in sample weights. Corrections for differences in relative production times and decay times were applied.

The corrected counting results obtained for gold and uranium spiked samples are given in Tables I and II The spiking of this very low grade material is lacking in uniformity, as the experimental standard deviation (σ_{exp}) of the count-rate values (column 5 in Tables I and II) is larger than the standard deviation due to counting statistics (σ_{cs}, column 4 in Tables I and II) In using a linear least-squares fit FORTRAN IV program, FITIT,[7,8] for the IBM-360, the values for σ_{exp} were used to obtain weighting of each mean count-rate (weight $= 1/\sigma_{exp}^2$) in the fitting procedure against the added gold or uranium concentrations The results are given in section (*i*) of Tables III and IV

TABLE I —RESULTS OF THE ANALYSIS OF SPIKED GOLD ORE SAMPLES

Sample	Sample weight, *g*	Au added *ppm*	Corrected count, *cpm/g*	Mean, *cpm/g*
1	1·0071	Nil	189 ± 14*	174 ± 21†
2	1·1455		149 ± 8	
3	1·1908		183 ± 8	
4	1·2154	1·001	836 ± 16	808 ± 30
5	1·3745		823 ± 15	
6	1·307		807 ± 15	
7	1·3224		766 ± 10	
8	1·1351	1·998	1464 ± 13	1394 ± 66
9	1·2438		1317 ± 11	
10	1·2637		1431 ± 10	
11	1·1563		1365 ± 11	
12	1·1870	4·000	2659 ± 20	2749 ± 195
13	1·1072		2951 ± 22	
14	1·2842		2521 ± 19	
15	1·1385		2864 ± 23	

* The error quoted is the standard deviation due to counting statistics (σ_{cs}).

† The error quoted is the experimental standard deviation of the count-rate values (σ_{exp})

The application of the FITIT program to all the count-rates obtained is also reported [Tables III and IV, section (*ii*)] In this approach the error due to the counting statistics, including the back-ground, was used to calculate the weighting for each point (weight $= 1/\sigma_{cs}^2$). This alternative approach to the fitting of results introduced larger weighting of the results for the less uniformly spiked samples and also introduced larger errors It is thus a less satisfactory approach although agreement within the errors is obtained, for gold and uranium, with the first approach. If better uniformity of spiking can be obtained it is expected that the extrapolated initial concentration obtained should be the same with both approaches.

For gold and uranium, the extrapolated concentrations obtained in our spiking and activation procedure are somewhat larger than the chemical assay values (see Table III and IV), although the errors quoted for the chemical values might be twice as large, as they depend very much on the analyst. In our spiking method better accuracy can be obtained by (*i*) increasing the methanol mixing period, (*ii*) taking special precautions in taking portions of the spiked samples for irradiation, (*iii*) taking caution in obtaining reproducible counting geometry (in our procedure the quartz tube with the sample was placed directly underneath the Ge-Li detector, as this had previously given satisfactory results[5])

TABLE II.—RESULTS OF THE ANALYSIS OF SPIKED URANIUM ORE SAMPLES

Sample	Sample weight, *g*	U added *ppm*	Corrected count, *cpm/g*	Mean, *cpm/g*
1	1·3200	Nil	322 ± 12*	334 ± 17†
2	1·2557		346 ± 15	
3	1·1997	60·0	1086 ± 17	1141 ± 55
4	1·1680		1213 ± 16	
5	1·2352		1113 ± 17	
6	1·3038		1152 ± 16	
7	1·1475	119·9	2070 ± 21	2038 ± 147
8	1·3467		1931 ± 19	
9	1·1975		1917 ± 19	
10	1·1140		2231 ± 15	
11	1·2761	240·3	3329 ± 22	3457 ± 103
12	1·2948		3572 ± 22	
13	1·3894		3431 ± 23	
14	1·3421		3496 ± 22	
15	1·2886	476·5	7451 ± 33	7027 ± 385
16	1·3131		6924 ± 31	
17	1·3702		6548 ± 27	
18	1·3252		7186 ± 32	

*† Errors as in Table I.

TABLE III.—DATA FROM PROGRAM FITIT USED FOR FITTING OF COUNT RATES *vs.* ADDED GOLD CONCENTRATIONS

(*i*) *Fitting of mean count-rate values*	
y at no gold addition ($x = 0$)	174·4 ± 9·0* cpm
Slope of straight line	626·4 ± 11·0 cpm per ppm Au
Calculated gold concentration in initial sample	$0{\cdot}27_8 \pm 0{\cdot}01_5$ ppm Au
(*ii*) *Fitting of all the count-rates obtained*	
y at no gold addition ($x = 0$)	161·1 ± 26·5 cpm
Slope of straight line	629·5 ± 15·3 cpm per ppm Au
Calculated gold concentration in initial sample	$0{\cdot}25_6 \pm 0{\cdot}04_2$ ppm Au

Chemical assay value of initial sample 0·202 ± 0·020 ppm Au.
* All errors quoted are standard deviations.

TABLE IV.—DATA FROM PROGRAM FITIT USED FOR FITTING OF COUNT RATES VERSUS ADDED URANIUM CONCENTRATIONS

(*i*) *Fitting of mean count-rate values*	
y at no uranium addition ($x = 0$)	334 ± 13 cpm
Slope of straight line	13·33 ± 0·28 cpm per ppm U
Calculated contents of uranium in orginal sample	25·1 ± 1·1 ppm U
(*ii*) *Fitting of all the count-rates obtained*	
y at no uranium addition ($x = 0$)	327 ± 74 cpm
Slope of straight line	13·67 ± 0·36 cpm per ppm U
Calculated contents of uranium in original sample	24·0 ± 5·2 ppm U

Chemical assay value of initial sample 19·5 ± 2·0 ppm U.
* Errors quoted are standard deviations.

Loss of added gold or uranium by possible preferential adhesion to the sides of the mortar can be discounted

CONCLUSION

For both elements, gold and uranium, the spiking plus neutron-activation procedure gives larger values for very low grade ores than those obtained by chemical assay The errors involved do not make possible any clear decision on this discrepancy but with further development of the technique this method of spiking and non-destructive analysis holds promise of application in the analysis of numerous types of low grade ore samples, as at present being done in this laboratory.

Atomic Energy Board
Pelindaba, Pretoria, S Africa

P. W. de Lange®
W. J. de Wet
J. H. Venter

Summary—In applying non-destructive neutron-activation analysis for gold and uranium in spiked low-grade ore samples, the following extrapolated unspiked concentrations were measured: $0{\cdot}27_8 \pm 0{\cdot}01_5$ ppm gold (chemical assay. $0{\cdot}20_2 \pm 0{\cdot}02_0$ ppm gold); $25{\cdot}1 \pm 1{\cdot}1$ ppm uranium (chemical assay value $19{\cdot}5 \pm 2{\cdot}0$ ppm uranium). Different approaches to the fitting of results, and the influence of spiking non-uniformity, are discussed

Zusammenfassung—Bei der zerstorungsfreien Neutronenaktivierungsanalyse auf Gold und Uran in gespickten armen Erzproben wurden folgende extrapolierte ungespickte Konzentrationen gemessen: $0{,}27_8 \pm 0{,}01_5$ ppm Gold (chemische Analyse: $0{,}20_2 \pm 0{,}02_0$ ppm Gold), $25{,}1 \pm 1{,}1$ ppm Uran (chemische Analyse: $19{,}5 \pm 2{,}0$ ppm Uran) Verschiedene Wege zur Anpassung der Ergebnisse sowie der Einfluß der nicht gleichmaßigen Spickung werden diskutiert

Résumé—En appliquant l'analyse par activation de neutrons non destructive à l'or et à l'uranium dans des échantillons de minerais apiciformes à faible teneur, on a mesuré les concentrations extrapolées non apiciformes suivantes $0{,}27_8 \pm 0{,}01_5$ p.p m. d'or (essai chimique· $0{,}20_2 \pm 0{,}02_0$ p.p m. d'or), $25{,}1 \pm 1{,}1$ p.p.m. d'uranium (valeur de l'essai chimique $19{,}5 \pm 2{,}0$ p.p m. d'uranium) On discute de différents accès vers l'ajustage des résultats et de la non-uniformité de répartition des aiguilles

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Talanta, 1968, Vol 15, pp 1493 to 1494 Pergamon Press Printed in Northern Ireland

LETTERS TO THE EDITOR

Ceramic crucibles for thermogravimetric analysis

SIR,

Results of thermoanalysis are known to be influenced by experimental conditions, *i.e* , by the rate of heating, the weight of the sample, the grain size, the degree of compacting, the gas atmosphere, *etc*. In DTA investigations in which the sample is placed in a sample holder instead of a boring, the shape, the wall thickness and the heat conductivity of the crucible holding the sample also influence the results However, the literature on thermoanalysis, and particularly on thermogravimetry, contains relatively little information on the role of the material of the sample holder, and on its effect on thermal processes.

Generally, platinum crucibles are used in thermoanalytical investigations However, platinum has, besides its known advantageous properties, certain disadvantages (it forms alloys with many substances and molten metals, its cleaning poses problems with glazing or vitrifying substances)

For thermogravimetric analysis, various sample holders made of ceramics or quartz have been used These sample holders have not found general application, because the walls of the crucibles were thick, and in most cases not uniform, which may cause errors in thermogravimetric measurements, particularly in complex thermoanalytical investigations, where two different thermal decomposition curves, *e g* , the TG and the DTA curves are recorded simultaneously with the derivatograph.

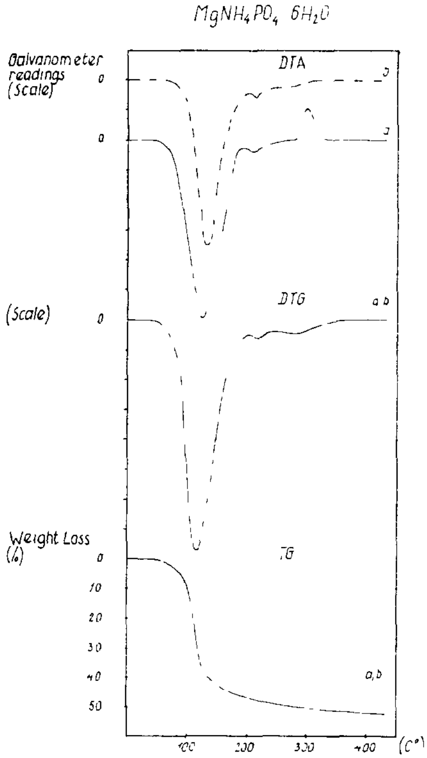

FIG 1

In our investigations, uniform, heat-resistant ceramic crucibles with thin walls (0.5 mm) were required. We succeeded in preparing such crucibles from sintered metal oxide ceramics. The process has been developed to permit routine manufacture of the crucibles.

The comparison of these ceramic crucibles with platinum crucibles showed that the results of thermal analysis may be influenced by platinum crucibles. In the derivatographic investigation of some components of nephroliths,[1] *e.g.*, in that of magnesium ammonium phosphate, an exothermic process was observed at about 300°, which could not be evaluated quantitatively on the basis of the protracted TG curve. This phenomenon was met only when a platinum sample holder was used and the derivatogram was recorded in air, without suction (Fig. 1, Curve *a*). This effect was absent when a ceramic crucible was used, or in experiments under an argon atmosphere, or when suction was applied (Curve *b*).

It is assumed that this phenomenon was caused by the oxidation of ammonia liberated during the decomposition. In the air atmosphere of the oven, any ammonia liberated remains in the vicinity of the crucible, and, owing to the large surface of the platinum crucible, may be oxidized at about 300°. This process is indicated on the DTA curve as an exothermic effect. It has been shown that this catalytic oxidation is influenced by the pretreatment of the platinum surface and by the area of the active platinum surface (ratio of the wall-area of the crucible to the weight of sample). Catalytic oxidation at this relatively low temperature of about 300° could also be found with other compounds which split off ammonia.[2]

This phenomenon seems of importance, since platinum crucibles are often used in thermal analysis. Catalytic oxidation on the walls of the platinum crucible can cause disturbances in the shape of the thermal curves, and difficulties in their evaluation.

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G. LIPTAY

Research Institute for Electricity
Budapest
22 April 1968

E. SÁRKÁNY

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Nomenclature of organic reagents of the arsenazo III group

SIR,

In recent years many workers have appeared on the analytical applications of arsenazo III and its analogues—2,7-bisazo-derivatives of chromotropic acid—of which there are more than 100.[1-6] It therefore seems to me that the time has come to agree on the nomenclature of this series, especially since different names have already been given to the same compounds. For example, 2,7-bis(2-sulphophenylazo)-1,8-dihydroxy-naphthalene-3,6-disulphonic acid is variously called orthanilic S,[1,3] and sulphonazo III.[4] 2,7-Bis(2-sulpho-4-nitrophenylazo)-1,8-dihydroxy-naphthalene-3,6-disulphonic acid is called nitrazo,[5] nitro-orthanilic S[1] and dinitrosulphonazo III.

In naming a reagent it is probably expedient to link the name with the constitution and the nature of the functional groups and substituents, but not with the character of its colour reactions or analytical applications, since in the first place the reagent usually interacts with several elements, and secondly it is always possible to expect to obtain more valuable reagents for given elements. The earlier names proposed for reagents, such as thoron, calciochrome, beryllon, palladiazo *etc.*, result in confusion when there is a choice of reagents for the element in question, especially when a study of the type of reagent is not being made. It may be that exceptions can be made for specially selective reagents, but only for a few.

For a given series of reagents synthesized from a single basic azo compound (*e.g.*, chromotropic acids) it is expedient that the name of the reagents should be characteristic of the nature of the diazo derivatives or of the salt-forming substituents *ortho* to the azo group, which are usually involved in the analytical functional groupings. Thus, taking tradition into account, the "arsenazo" reagents should contain at least one *o*-arson-*o*′-hydroxyazo group, the "orthanilic" series (based on orthanilic acid) should have at least one *o*-sulpho-*o*′-hydroxyazo group, and so on. A suffix may be added that

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Institute for Applied Chemistry
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Numerical designations, *e.g*, aminomethylazo III, are less logical because as a rule the compound I and II have either not been synthesized or are of no analytical interest It must be observed that it is not, of course, necessary to look for names for reagents which have no clear applications in analytical chemistry.

A proposed nomenclature for the arsenazo III series is given in Table I

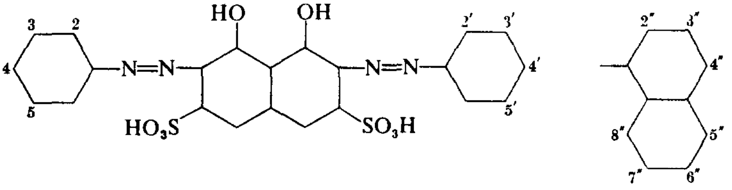

TABLE I

	Proposed names	
Reagent substituents	English	Russian
2,2′-di-AsO_3H_2	arsenazo III	арсеназо III
2-AsO_3H_2, 3′-SO_3H	arsenazo M	арсеназо M
2-AsO_3H_2, 3″,8″-di-SO_3H	arsenazo AE	арсеназо AE
2,2′-di-PO_3H_2, 4,4′-di-Cl	chlorophosphonazo III	хлорфосфоназо III
2-COOH	anthranilic B	антраниловый Б
2,2′-di-SO_3H	orthanilic S	ортаниловый C
2,2′-di-SO_3H, 4,4′-di-NO_2	nitro-orthlanilic S	нитроортаниловый C
2-SO_3H, 2′-COOH	orthanilic K	ортаниловый K
2,2′-di-OH, 3,3′-di-SO_3H, 5,5′-di-Cl	sulphochlorophenol S	сульфохлорфенол C
2-OH, 3,3-di-SO_3H, 5-NO_2,	sulphonitrophenol M	сульфонитрофенол
2,2 -di-OH, 3,3′,5,5′-tetra-NO_2	picramine S	пикрамин C
4,4′-di-NO_2	4-nitrophenyl S	4-нитробензол C
3′-SO_3H (first diazo component amino-antipyrine)	antipyrine M	антипирин
Both diazo components aminopyridine	pyridine S	пиридин C

Vernadsky Institute for Geochemistry and Analytical Chemistry
Academy of Sciences, Moscow
S B. SAVVIN

23 *March* 1968

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Editorial note. The problem is further complicated by the difficulty of transliteration from Russian to English or *vice versa*. For example ортаниловый should be translated *ortanilic*, but the *h* must be inserted to made the derivation recognizable in English. Worse, бензол is used in Russian for the grouping generally referred to as *phenyl* in English, and a translation is needed instead of merely transliteration.

Talanta

An International Journal of Analytical Chemistry

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EDITOR'S FOREWORD

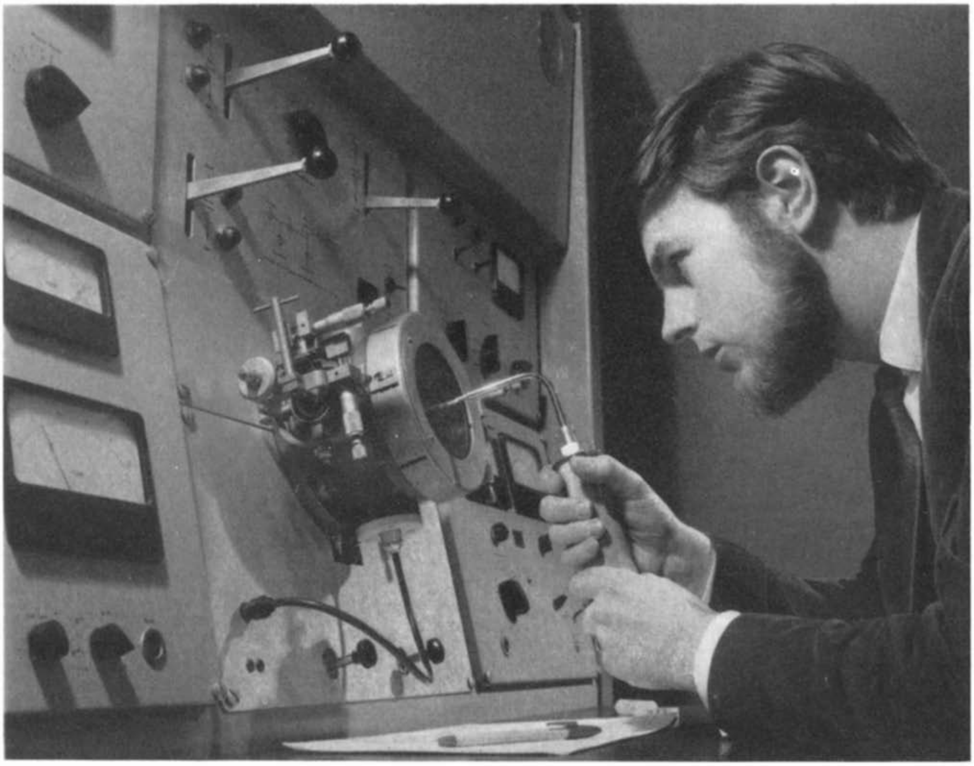
On Monday, November 3rd, 1947, A. A. SMALES started work at the Atomic Energy Research Establishment, Harwell. The Editorial Board and Publishers of *TALANTA* take pleasure in honouring 21 years of signal achievement and wishing him every success in the future by presenting this special issue, which is comprised entirely of invited contributions from present and former colleagues and associates.

A. A. SMALES, O.B.E., D.Sc., F.R.I.C.

A view of the Atomic Energy Research Establishment at Harwell in March 1946.

The new Analytical Science Laboratory, Harwell, 1968.


MICROPROBE



The Analytical and Research Development Unit was formed 20 June 1968 to provide industry with direct access to Harwell expertise and resources. The latter include a Laser microprobe (left) and a Spark source mass spectrograph (above).

Talanta, 1968, Vol. 15, p. i. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Étude polarographique et physicochimique de *N*-oxydes—I. Mécanisme de la réduction et hydration des formylpyridines *N*-oxydes: E. Laviron and R. Gavasso (2 *July* 1968)

Anwendung der Röntgenfluorezenz in der Spurenanalyse—II. Anreicherung von Spurenmetallen durch Fällung mit 1-(2-pyridylazo)-2-naphthol (PAN): Richard Püschel (23 *July* 1968)

Thermal study of some organo–lead compounds: S. R. Garg and R. S. Rai (24 *July* 1968)

Elements de fluorimetrie organique fonctionelle—II: M. Pesez and J. Bartos (25 *July* 1968)

Spectrophotometric determination of beryllium by Methylthymol Blue—a critical study: K. C. Srivastava and S. K. Banerji (28 *July* 1968)

Determination of small amounts of TBP and DBP in uranyl nitrate solutions: Tomitaro Ishimori and Kaoru Ueno (29 *July* 1968)

1,5-Bis(dicarboxymethylaminomethyl)-2,6-dihydroxynaphthalene as a selective spectrofluorimetric reagent for calcium: B. Budĕšínsky and T. S. West (31 *July* 1968)

Oxygen isotope fraction factor between CO_2 and Co_3^{2-}: S. K. Sharma and T. Sharma (31 *July* 1968)

Komplexe der Anthranil-*N*,*N*-diessigsaure mit tetravalenten Metallen—I. Zirconium und Hafnium: C. Dragulescu, Septimia Policec and T. Simonescu (31 *July* 1968)

Influence of non-aqueous solvents on the equivalence point determination in acid–base neutralization reactions—I: The titration of weak bases with periodic acid: Walentyna Ruskul (31 *July* 1968)

Mass spectrometry of volatile mercury salts: J. R. Majer (2 *August* 1968)

Spectrophotometric determination of chlorate ion in the presence of large excess of halide ions: P. M. Maguire and H. E. Rubalcava (2 *August* 1968)

Oxygen determinations with the aluminium corrosion electrode: E. Scarano and M. Mascini (2 *August* 1968)

Phosphorescence characteristics of several antimetabolites: L. B. Sanders, J. J. Cetorelli and J. D. Windfordner (6 *August* 1968)

Extractive photometric determination of vanadium with a catechol and tertiary amine system: Vĕnceslav Patrovský. (6 *August* 1968)

Investigation of vicinal dioximes as gravimetric reagents for metals: L. S. Bark and D. Brandon (8 *August* 1968)

Some vicinal dioximes as reagents for palladium: L. S. Bark and D. Brandon (8 *August* 1968)

Spectrophotometric determination of selenium with cyclohexanone: M. S. Cresser and T. S. West (20 *August* 1968)

***N*-Acetylsalicyloyl-*N*-phenylhydroxylamine as an analytical reagent. Spectrophotometric determination of titanium(IV):** Joy Joseph and C. P. Savariar (20 *August* 1968)

Talanta, 1968, Vol. 15, p. i. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Die Analyse der Luft und ihrer Verunreinigungen: W. LEITHE. Wissenschaftliche Verlagsgesellschaft mbH, Stuttgart, 1968. Pp. xiii + 288. DM 58.

The author, who is head of the laboratories of the Österreichische Stickstoffwerke in Linz, has very ably covered the fields of atmospheric pollution and the analysis of air for a wide range of contaminants. His own wide experience has resulted in a collection of methods and techniques with much useful practical information and many valuable comments. The notes on the industrial significance and the physiological activity of many compounds makes interesting reading. There are sections on Atmospheric pollution, Sampling techniques, Analysis of artificial mixtures, Instrumental methods for inorganic contaminants and for organic contaminants, and an Appendix with MAK-Werte and MIK-Werte (maximum allowed concentrations at the workbench, and in exhaust gases). A very useful book which should find a place on every industrial analyst's shelf.

Polarography—Plenary Lectures from the I.U.P.A.C Congress, Kyoto, 1966. Butterworths, London, 1967. Pp. 124. 50s.

Seven plenary lectures, also published in *Pure Appl. Chem.*, 1967, **15**, No. 2, are here presented in book form. The topics covered are Theory of polarographic currents, Polarography in molten salts, Theory of the current in a.c. polarography, Adsorption of organic substances on the free water surface and at the water–mercury interface, Polarographic methods of analysis (in particular, stripping methods), Recent trends in organic polarography, and Advances in a.c. polarography and tensammetry. These are review-type articles and offer useful background reading to the subject. More careful editorial supervision might have eliminated a number of obvious mistakes and ambiguities.

Radio and Electronic Materials: N. P. BOGORODITSKII and V. V. PASYNKOV. Iliffe, London, 1967. Pp. 350. 63s.

This is a translation of the original Russian book on materials science for radio and electronic engineers, and is in two parts—on dielectrics, and on conductors, semiconductors, and magnetic materials. There is a strong chemical bias to the theoretical sections, and the applied sections contain many examples of practical devices. The whole book is well illustrated with very many figures and diagrams. This will be a useful reference book for any chemist working in the electronics industry, as well as being suitable reading for students of electrical engineering.

Substoichiometry in Radiochemical Analysis: JAROMÍR RŮŽIČKA and JIŘÍ STARÝ. Pergamon, Oxford 1968. Pp. xi + 151. 55s.

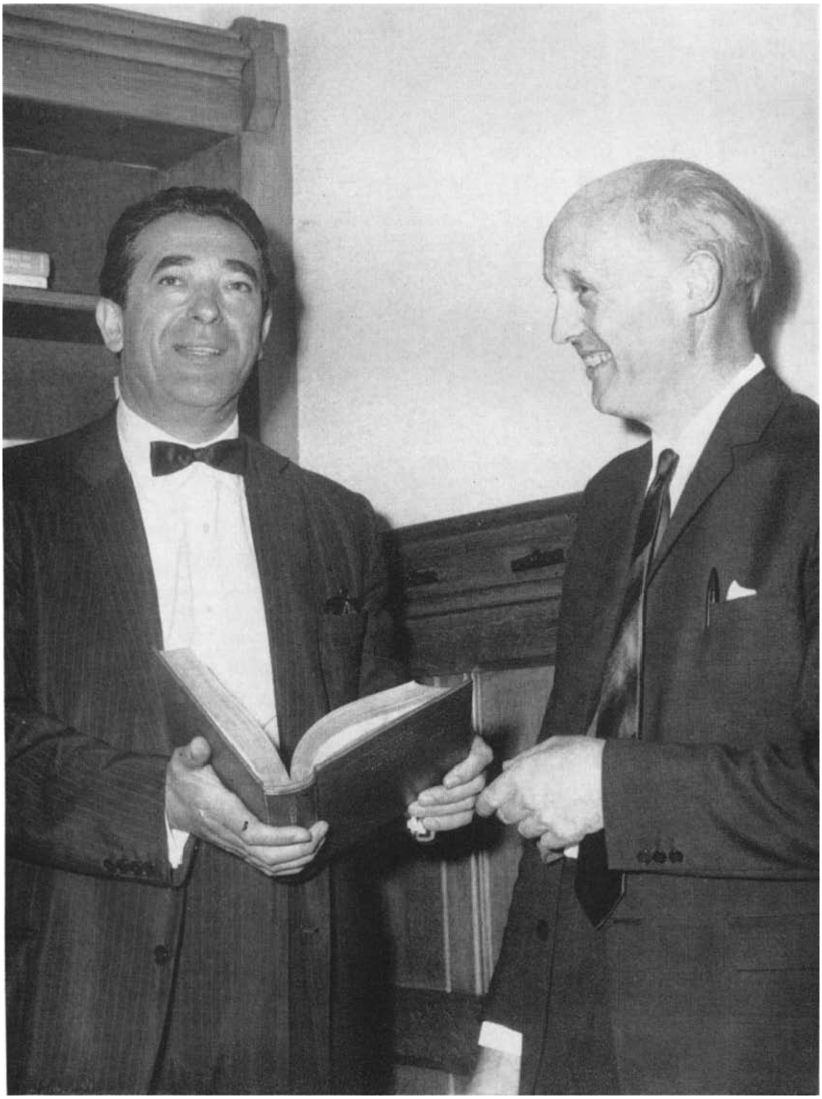
An authoritative guide to the substoichiometric principle and its applications, by the originators of the technique. The compilation of procedures is particularly useful, and the burden of the second sentence of the preface should be taken to heart by all chemists.

Trace Inorganics in Water: Advances in Chemistry Series, No. 73: Editor ROBERT F. GOULD. American Chemical Society, Washington D.C., 1968. Pp. viii + 396. $12.50.

This volume contains the full text of the 21 contributions to a symposium held in 1967 on various aspects of the chemistry of traces of inorganic substances in water. The result is a collection of extremely wide-ranging papers which could be read with profit by chemists of all types, and not least by students. The topics (selected almost at random in this notice) range from entropy effects, through atomic-absorption and atomic-fluorescence spectroscopy, to concentration of solutions by freezing.

Louis Gordon Memorial Award 1967

MR. ROBERT MAXWELL, M.P., Chairman of Pergamon Press, presents a specially bound copy of *Talanta* 1967 to PROFESSOR H. J. V. TYRELL (right), whose paper "End-point Sharpness in Thermometric Titrimetry" (1967, **14,** 843) was adjudged the best-written, stylistically, of the year. The presentation was made at the House of Commons, London, on 16th July.



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EDITORIAL

HOW MANY km TO BABYLON?

WE are sure that all *Talanta* readers can safely be assumed to be thoroughly conversant with current scientific literature and to be aware of the recommendations that all scientific publications should use metric (S.I.) units exclusively. For analytical chemists the changes will be very few. With the redefinition of the litre as 1 dm^3, the new ml will differ from the old by a factor of 1.000028, a difference which is far too small to affect anything but atomic weight work. The main changes appear to be the use of nm instead of $m\mu$ and of Hz instead of c/s, but the greatest effect will come from the conversion of non-metric into metric units. Henceforward, dimensions of apparatus will be given in S.I. units and not in feet and inches. In making the conversion, authors must use a realistic number of significant figures in the factor used; a good working rule for use with apparatus that must be made in the workshop would be to assess the working tolerance of machining or other fabrication, work out the number of significant figures implied by it for the particular dimension, use one more than this number of digits in the conversion factor, and round off the answer to the same degree of tolerance as in the original dimensional units. For non-critical dimensions, of course, such as the size of a well-type crystal in a scintillation counter, a similar rule can be used, and a 3 × 3 in. crystal would have a 75 × 75 mm metric equivalent (the use of the cm as a unit of length is not normally permitted).

There is one problem, however, which is not tackled by the S.I. system, and that is the difference between the American and the European billion (10^9 and 10^{12} respectively). Fortunately there is a perfectly respectable and well-known term for 10^9, the milliard, and we propose to use this to avoid the confusion that can arise from unqualified use of "billion". As an abbreviation for milliard we propose to use M, which avoids confusion with m for million or metre, and with M for molar; parts per milliard (a common concentration unit in trace analysis and pollution studies) will be ppM, and parts per million will be ppm as before. No confusion should arise with M for mega, which can be used only as a qualifying prefix to a unit.

OBITUARY

ANATOLII KYRILLOVICH BABKO

It is with regret that we announce the sudden death in Kiev, on 7th January 1968, of ANATOLII KYRILLOVICH BABKO. Professor Babko, of the Ukrainian Academy of Sciences, was well known for his work on the analytical chemistry of complex compounds, a field of research to which he had made many contributions, one of the last of which was a review on ternary complexes, which will be published in *Talanta*.

Talanta, 1968, Vol. 15, p. i. Pergamon Press. Printed in Northern Ireland

NOTICES

1–5 *April* 1968

Thermal Analysis School. The Thermal Analysis Group of The Society for Analytical Chemistry is holding a residential thermal analysis school at the Cement and Concrete Association's Conference and Training Centre, Fulmer Grange, Slough, Bucks. on 1–5 April 1968. Lectures by leading workers in the field, practical work on a wide range of thermal analysis equipment loaned by various manufacturers, and discussion groups on specialist topics will help senior scientists and technologists to evaluate critically the use of thermal analytical techniques in relation to their own testing and research requirements. Details of the study programme and course arrangements may be obtained from The Thermal Analysis School, Cement and Concrete Association Training & Conference Centre, Fulmer Grange, Slough, Bucks., U.K.

7–11 *April* 1968

EUCHEM Conference on Problems of Non-stoichiometry, Schloss Elmau, near Mittenwald, Germany.

The following topics will be dealt with

The Chemistry of Non-stoichiometric Phases
Crystallographic Aspects of Non-stoichiometric Phases
Thermodynamics of Non-stoichiometric Phases
Valence Chemistry of Compounds of Transition Elements
Methods of Investigation.

The provisional programme as well as the preliminary registration forms may be obtained from Gesellschaft Deutscher Chemiker, 6000 Frankfurt (M), Postfach 9075, Germany, who are organizing the conference.

ADDENDUM

C. E. PLOCK and W. S. POLKINGHORNE: Controlled potential coulometric determination of uranium and neptunium in uranium–neptunium alloys, *Talanta*, 1967, **14**, 1356.

The date of receipt of the above article was as follows.

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Talanta, 1968, Vol 15, pp 1 to 11 Pergamon Press Printed in Northern Ireland

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An electrical detection system for a spark source mass spectrograph: R J Conzemius and H. J. Svec (7 *August* 1968)

Logarithmic converter for atomic-absorption spectrometry: Michael D Morris and James B. Orenberg (12 *August* 1968).

A cell for high-precision constant-current coulometry with external generation of titrant. High-precision assay of potassium hydrogen phthalate and of potassium dichromate: John Knoeck and Harvey Diehl (13 *August* 1968)

L'application de l'absorption indirecte des neutrons pour une rapide determination du contenu de phosphore dans les apatites et les engrais phosphores: Marek Brafman, Nelli Biala, Joachim Kierzek, Marek Lelental and Karol Akerman (19 *August* 1968)

Spectrophotometric studies on surfactant–dye interaction: Wahid U Malik and Puran Chand (22 *August* 1968)

Potassium thiocarbonate as a complexing agent and precipitant: K N Johri, N. K Kaushik and Kirpal Singh (23 *August* 1968)

Determination of silver by potentiometric titration with sodium thiosulphate: Ray E Humphrey (29 *August* 1968)

Spectrophotometric determination of copper in plutonium metal with 2,9-dimethyl-1,10-phenanthroline: J W Lindsay and C E. Plock (30 *August* 1968)

2(6-Methylpyridyl)amidoxime, a sensitive reagent for copper: J. R Pemberton and H Diehl (3 *September* 1968)

Phenyl-2-(6-methylpyridyl)ketoxime—a reagent for copper in strong alkalies: J R Pemberton and H Diehl (3 *September* 1968)

High sensitive extraction–photometric method for nickel with dithizone and phenanthroline: K S. Math, K S Bhatki and H Freiser (3 *September* 1968)

Investigation of the diethyldithiocarbamates of palladium, including the determination of their stability constants: G B Briscoe and S. Humphries (9 *September* 1968)

Determination of hydrazine by gas evolution: C P Lloyd and W. F. Pickering (9 *September* 1968)

Inorganic analysis in organic solvents—III. Adsorption characteristics of metal chelate compounds on aluminas and silica gels: M P T Bradley and D A Pantony (10 *September* 1968)

Manganese(IV): A new oxidimetric titrant: Gary L Silver (10 *September* 1968)

Cation-exchange behaviour of several elements in hydrobromic acid–organic solvent media: J Korkisch and E Klakl (11 *September* 1968)

Determination of small quantities of xanthate: C Pohlandt, E B T Cook and T W Steel (11 *September* 1968)

Dissociation constants of Alizarin Fluorine Blue: C K Laird and M A Leonard (11 *September* 1968)

Studies of the ceric ion oxidation of α-mercaptocarboxylic acids, by thermometric titrimetry: W A. Alexander, C J Mash and A McAuley (11 *September* 1968)

Infrared determination of calcium or lithium nitrate in acetone solution; determination of calcium or lithium in the presence of strontium or barium: G Norwitz and D E Chasan (12 *September* 1968)

Rapid method with an enhanced stability for the spectrophotometric determination of calcium with glyoxal bis(2-hydroxyanil): Jacob Lapid and Yechiel Pickholtz (13 *September* 1968)

Microdetermination of the nitrates and the nitramines—I. Titrimetric method based on reduction with iron(II), titanium(III), and a mixture of both: William Ibrahim Awad and Saad S M Hassan (13 *September* 1968)

Microdetermination of the nitrates and the nitramines—II. Gasometric methods based on reduction with mercury, iron(II) and titanium(III): William Ibrahim Awad and Saad S M Hassan (13 *September* 1968)

Microdetermination of nitrates—III. Gasometric method based on a new redox reaction with hydroquinone: William Ibrahim Awad and Saad S M. Hassan (13 *September* 1968)

Determination of isotopic radium in thorium mill effluents: V A Kamath and P P. Parekh (13 *September* 1968)

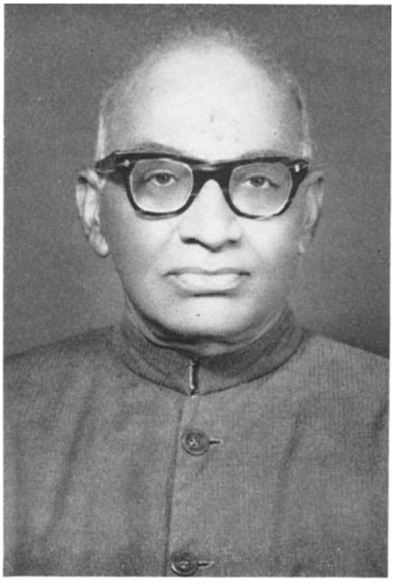
Complexation of scandium with 3,5,6,7,3′,4′-hexahydroxyflavone (quercetagetin) and its application to spectrophotometric determination of scandium: B P Gupta, R P Singh, D K Bhardwaj and Mohan Katyal (16 *September* 1968)

Spectrophotometric determination of zirconium and other colour reactions with rutin: B. S Garg, R. P. Singh and Mohan Katyal (16 *September* 1968)

Coloured chelate of palladium(II) with Eriochromecyanine RC: Suresh C Shrivastawa, Kailash N. Munshi and Arun K. Dey (16 *September* 1968)

Spectrophotometric determination of L-ascorbic acid: Yoshiro Ogata and Yoshio Kosugi (16 *September* 1968)

PROFESSOR G. GOPALA RAO



Gandikota Gopala Rao, Head of the Department of Chemistry, Andhra University Waltair (India), completes 60 years of life on 11 November 1968. He had his early education at Rajah's College, Kakinada and Maharajah's College, Vizianagaram, where he received the Bachelor's degree with distinction and gold medal. He then proceeded to Allahabad where he took the M.Sc. degree in 1930, receiving the Victoria Jubilee medal for first place. With a fellowship offered by Andhra University, Gopala Rao took up research work under Professor Dhar. On the opening of Honours courses in Chemistry in 1932 by Andhra University, he was made lecturer, and rising to be reader (1938), professor (1946) and head of department (1949), he chose an academic career, rejecting alluring offers from industrial and research establishments.

The scientific work of Gopala Rao is largely in the area of redox analytical processes. His early interest in photochemistry led him to the development of new analytical processes by application of the chemical action of light. This work demanded an oxidant for the determination of reductants without interference from the excess of organic compounds added as photochemical reductants. Thus was discovered the specific use of sodium metavanadate.

Another field which has interested Gopala Rao and school is the use of catalysts in analytical chemistry, and many methods have resulted from this work. His work on redox reactions in concentrated orthophosphoric acid medium has opened a new area of redox titrimetry, iron(II) then being a more powerful reductant, and the "normal" redox reactions being reversed. He has also demonstrated that potassium dichromate becomes a more useful and convenient oxidant in phosphoric acid medium. Publication of these results in a series of papers in *Talanta* has attracted worldwide attention. Professor Gopala Rao is currently engaged in the investigation of the kinetic and other fundamental aspects of these redox reactions.

Other work includes investigation of ascorbic acid, hydrazine, and arsenic(III), extensions of the use of cerium(IV), chlorate, iodate and iron(III) as oxidimetric reagents, introduction of new redox indicators (metal phthalocyanins) and extensions of the use of triphenylmethane dyes, cacotheline, ferroin and diphenylamine derivatives as redox indicators.

While taking an active part in chemical research, he also loves to organize. Besides extending the inorganic, organic and physical chemistry sections, he has added analytical and nuclear chemistry sections to the department. Under his leadership, Andhra University started in 1957 a course leading to the M.Sc. degree in Analytical Chemistry. During 1944-49 he helped the Madras State Government to develop an Analytical and Testing Laboratory of which he was the honorary director. He has served as *Talanta* regional editor for India and Pakistan. In 1963 he became Principal of the University colleges. He has afforded ample opportunities to his younger colleagues in the department to engage in active research in different areas of chemistry. Over 30 persons have taken their D.Sc. and Ph.D. degrees under him and many of them occupy important positions in the Universities, research laboratories and industry.

M. N. SASTRI

Talanta, 1968, Vol. 15, pp. i to ii. Pergamon Press. Printed in Northern Ireland

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Effect of chromium (III) and of other ions on the absorptiometric determination of copper with 2,2′-biquinolyl: H. M. N. H. Irving and W. R. Tomlinson. (20 *February* 1968)

Uranium and thorium abundances in chondritic meteorites: J. W. Morgan and J. F. Lovering. (26 *February* 1968)

Potassium-argon dating of the Cape Granite and a granitized xenolith at Sea Point: G. D. L. Schreiner, H. H. Basson and A. A. Verbeek. (8*April* 1968)

Occurrence of bromine in plants and soil: Yoshio Yamada. (23 *April* 1968)

Semipermeable ion-exchange membranes as a preconcentration matrix for trace analysis by electrochemical and neutron-activation techniques. Applicability and limitations: Uri Eisner and Harry B. Mark, Jr. (26 *April* 1968)

Determination of antioxidants in polymeric materials: D. A. Wheeler. (26 *April* 1968)

Potentialities of infrared spectroscopy in determining traces of carbon or oxygen as carbon dioxide: T. Carter and H. I. Shalgosky. (29 *April* 1968)

Reactions between mercury (II) and organic compounds—V. Study on the complex of mercury (II) with *o*-(2-thiazolylazo) resorcinol: Fumiaki Kai. (29 *April* 1968)

Anwendung von Extraktionsverfahren in der inversen Voltammetrie (I): H. Matschiner and M. Roschig. (29 *April* 1968)

Computer calculation of equilibrium constants of species present in mixtures of metal ions and complexing agents: I. G. Sayce. (29 *April* 1968)

Extraction of vanadium into isobutyl methyl ketone: Application to the determination of vanadium by atomic-absorption spectroscopy: Hans J. Crump-Wiesner and William Purdy. (30 *April* 1968)

Diffusion of fluoride in hexamethyldisiloxane: R. J. Hall. (30 *April* 1968)

Determination of chromium and aluminium in a 'nimonic' alloy by activation with fast neutrons: D. A. Quigley and J. W. A. Trussler. (2 *May* 1968)

On the nomenclature of organic reagents of the arsenazo III group: S. B. Savvin. (2 *May* 1968)

Reactions between mercury (II) and organic compounds—VI. New indicator for the determination of mercury (II): F. Kai (2 *May* 1968)

Gravimetric determination of nickel with quinoxaline-2,3-dithiol by precipitation from homogeneous solution: J. A. W. Dalziel and A. K. Slawinski. (3 *May* 1968)

Polarographic behaviour of the complexes of cadmium and lead with benzilic acid: J. K. Gupta and C. M. Gupta. (3 *May* 1968)

Collection of traces of metals on carboxycellulose cation-exchanger: E. Schulek, Zs. Remport-Horváth, A. Lásztity and E. Körös. (3 *May* 1968)

Ceramic crucibles for thermogravimetric analysis: G. Liptay and E. Sárkány. (6 *May* 1968)

A scandium generator: M. Y. Mirza and A. Aziz. (6 *May* 1968)

Trace analysis by atomic-absorption spectrophotometry—a sequential multi-element approach by solvent extraction: B. Montford. (7 *May* 1968)

Determination of ultra-micro amounts of selenium by electron-capture detector gas chromatography: Susumu Nakashima and Kyoji Toei. (8 *May* 1968)

Separation and solvent extraction of vanadium and uranium with n-propyl 3,4,5-trihydroxybenzoate: Fadil Jasim. (8 *May* 1968)

Cation-exchange separation of hafnium and zirconium from accompanying metal ions: J. Korkisch and K. A. Orlandini. (8 *May* 1968)

Simple method for the thermoanalytical observation of processes involving the splitting-off of ammonia or halogen: Mihály Berényi. (13 *May* 1968)

Kinetic study of consecutive reactions by the same-absorbance method: R. S. Roy. (13 *May* 1968)

Some variables affecting a proposed X-ray fluorescence solution method of analysis for titanium alloys: G. L. Vassilaros and J. P. McKaveney. (14 *May* 1968)

Spectroscopy in separated flames—V. The properties and application of argon- or nitrogen-sheathed nitrous oxide–acetylene flames in flame emission spectroscopy: G. F. Kirkbright, M. Sargent and T. S. West. (14 *May* 1968)

Polarography as a tool in organic analysis. The simultaneous microdetermination of bromine–iodine and chlorine–iodine in organic compounds after oxygen flask combustion: Y. A. GAWARGIOUS, G. M. HABASHY and B. N. FALTAOOS. (14 *May* 1968)

Fluorescence characteristics in inorganic complexes in hydrochloric acid medium at liquid nitrogen temperature: G. F. KIRKBRIGHT, C. G. SAW and T. S. WEST. (14 *May* 1968)

Coulometrische Metallometrie: Elektrolytisch erzeugter Kupriion als coulometrischer Titrant: PANTA S. TUTUNDŽIĆ and MILAN M. PAUNOVIĆ. (14 *May* 1968)

Talanta, 1968, Vol. 15, pp. i to ii. Pergamon Press. Printed in Northern Ireland

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Solubility of water in hydrocarbons as a function of water activity: J. W. Roddy and C. F. Coleman (29 *January* 1968)

Neutron-activation analysis for the study of metallogenic provinces: Ernst A. Uken, Gabriel G. Santos and Richard E. Wainerdi. (2 *February* 1968)

Determination of hafnium by neutron activation, and variation in the Zr/Hf ratio of some granite masses: J. Esson, P. Hahn-Weinheimer and H. Johanning. (5 *February* 1968)

Chemical analysis of ceramic materials, containing uranium and plutonium, arising from the development of nuclear fuels: G. W. C. Milner, G. Phillips and A. J. Fudge. (9 *February* 1968)

Solvent extraction of Hf(IV) by *N*-benzoyl-*N*-phenylhydroxylamine: K. F. Fouche. (16 *February* 1968)

Development and influence of autoanalysers and data processing in analytical chemistry: L. E. Smythe. (27 *February* 1968)

Use of neutron-energy moderation for resolving interferences in fast-neutron activation analysis: T. B. Pierce, J. W. Edwards and K. Haines. (29 *February* 1968)

Use of immersion-type fibre optics in photometry and automatic photometric titrations: M. G. Young, T. H. Clarke and R. T. Schlick. (14 *March* 1968)

Über Eisen(III)-Komplexe mit Phenolen—II. Chelate mit Salicylsäure- und Brenzcatechinderivaten: Gerhard Ackermann and Dieter Hesse. (17 *March* 1968)

Use of instrumental activation-analysis for the characterization of terrestrial and extra-terrestrial material: M. P. Menon and R. E. Wainerdi. (19 *March* 1968)

Determination of caesium-137 in fast-reactor coolant systems: G. Oldham, A. R. Ware and D. J. Sykes. (20 *March* 1968)

Spectrophotometric extractive titrations—VI. Titrations with 1-(2-pyridylazo)-2-naphthol: Aftanas Galik. (20 *March* 1968)

Spectrophotometric determination of some *vic*-diols: G. Nisli and A. Townshend. (23 *March* 1968)

Complexes mixtes des nitrilotriacetates metalliques avec l'acide glutamique ou avec l'acide aspartique: J. Israili and M. Cecchetti. (25 *March* 1968)

Indirect complexometric semi-micro determination of iodide: D. Nonova and S. Popandova. (25 *March* 1968)

Spectrophotometric study of the reaction of magnesium(II) with arsenazo III: Rahila Doicheva and Maria Koeva. (26 *March* 1968)

Spectroscopy in separated flames—IV. Application of the nitrogen-separated air–acetylene flame in flame-emission and atomic-fluorescence spectroscopy: R. S. Hobbs, G. F. Kirkbright, M. Sargent and T. S. West. (26 *March* 1968)

Potentiometric studies of the complexes of chromium(VI). Molybdenum(VI) and tungsten(VI) with some Azoxine S dyes: S. S. Goyal and J. P. Tandon. (28 *March* 1968)

Carboxyarsenazo and Dibromosulphonazo III as selective and sensitive reagents for the spectrophotometric determination of palladium: J. G. Sen Gupta. (1 *April* 1968)

Germanomolybic acid and basic organic dyestuffs—I. Spectrophotometric determination of Ge(IV) with xanthenic dyestuffs: Gr. Popa and L. Paralescu. (1 *April* 1968)

Thiovioluric acid as an analytical reagent—I. Gravimetric determination of palladium: R. S. Chawla, Yag Dutt and R. P. Singh. (4 *April* 1968)

Spectrophotometric determination of tartrate in the presence of citrate: G. Nisli and A. Townshend (4 *April* 1968)

Use of a medium-dispersion instrument for the spectrochemical determination of thorium, yttrium and the rare earths in silicates: N. E. Cohen, R. D. Reeves and R. R. Brooks. (15 *April* 1968)

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Electrogravimetric trace analysis on a piezoelectric detector: James P. Mieure and Jerry L. Jones. (16 *April* 1968)

On potentiometric titration curves in complexometry: A. Hulanicki and M. Torjanowicz. (16 *April* 1968)

***p*-Nitroaniline as a colorimetric reagent for sulphur dioxide:** Per Olaf Bethge and Margareta Carlson. (16 *April* 1968)

Determination of metallic iron, ferrous oxide, and ferric oxide in admixture: B. R. Sant and T. P. Prasad. (17 *April* 1968)

Automated determination of traces of mercury in biological materials by substoichiometric radioisotope dilution: J. Růžička and C. G. Lamm. (17 *April* 1968)

Radiometric acid–base titrations: L. Erdey, O. Gimesi and F. Szabadváry. (17 *April* 1968)

Extraction determination of caesium in fission-products with a nitrobenzene solution of lithium dipicrylaminate: J. Krtil and M. Bezděk. (18 *April* 1968)

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Anionic liquid–liquid extraction of scandium by a long chain amine (Amberlite La-2) in acid-sulphate media: Tsuneo Shimizu (5 *December* 1967)

Determination of parts-per-billion concentrations of mercury by atomic-fluorescence flame spectrometry: T. J. Vickers and S P Merrick (5 *December* 1967)

Spectrophotometric determination of tetrafluoroborate with ferroin: Vernon S. Archer, Franklin G. Doolittle and Laverne M. Young (7 *December* 1967)

Nephelometric determination of gold with di-2-thienylketoxime: W. J Holland and J. Gerard (20 *December* 1968)

Homogeneous precipitation of nickel-salicylaldoximate by evaporation of mixed organic solvents: Mohsin Qureshi and Waqif Husain (21 *December* 1967)

Estimation of dimethylsulphoxide with chloramine-T: G. Aravamuden and D. Venkappayya (21 *December* 1967)

Activation analysis of selenium and tellurium trace impurities in gallium, arsenic and GaAs: H. Rausch and A. Salamon (21 *December* 1967)

Determination of nicotinic acid with gold chloride: O. C. Saxena (22 *December* 1967)

Improved method for the specific separation of selenium by solvent extraction with saturated monoketones: N. Jordanov and L. Futekov (22 *December* 1967)

Differential spectrophotometry of nickel as its pyridine-2,6-dicarboxylic acid complex: G. Den Boef and H. Poppe (22 *December* 1967)

Substoichiometric masking—II. The determination of traces of cobalt in metallic nickel and nickel salts: H. Flaschka and J. Garrett (22 *December* 1967)

Ion-exchange analysis of columbium alloys: T. A. Ferraro (28 *December* 1967)

Location and analysis of 2-deoxy sugars on chromatograms and pherograms by fluorescence: E. Sawicki, C. R. Engel, W. C. Elbert and K. Gerlach (2 *January* 1968)

Mass-spectrometric analysis of high-purity carbon dioxide: R. T. Parkinson and R. E. Wilson (5 *January* 1968)

Direct determination of boron in steel and nickel alloys: A. Tolk, W. A. Tap and W. A. Lingerak (8 *January* 1968)

Determination of sulphur in the low ppm range in uranium metal, uranium carbide, and other materials: Louis Silverman (8 *January* 1968)

Spectrophotometric studies of oximidobenzotetronic acid complexes with platinum metals—II. Determination of iridium(IV): G S Manku, A. N. Bhat and B. D. Jain (9 *January* 1968)

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Thermogravimetric analysis of molybdenum(VI) sulphide precipitated with potassium thiocarbonate and gravimetric determination of molybdenum(VI) in the presence of adverse ions: K. N. Johri and Kirpal Singh (9 *January* 1968)

Thermogravimetric analysis of the sulphides of selenium(IV), tellurium(IV) and vanadium(V) obtained with potassium thiocarbonate reagent and their gravimetric estimations: K. N. Johri and N. K. Kaushik (9 *January* 1968)

Thermometric titration of some monoprotic and diprotic acids in aqueous and non-aqueous media: R. J. Harries (10 *January* 1968)

Applications of enzyme-catalysed reactions in trace analysis—II. Determination of cyanide, sulphide and iodine using invertase: D. Mealor and A. Townshend (10 *January* 1968)

Determination of iron, nickel, chromium and vanadium by means of redox and ion-exchange columns: G. A. H. ROBERTS (10 *January* 1968)

Study of the reduction of rhenium(VII) with tin(II) ions in sulphuric acid medium, with respect to analytical application: N. JORDANOV and M. PAVLOVA (11 *January* 1968)

Suggestions for reporting thermoanalytical, thermogravimetric and derivatographic data: JERZY TRAU (12 *January* 1968)

Argentometric titration of hexacyanoferrate(II) using adsorption indicators: P. S. DUBEY and K. N. TANDON (12 *January* 1968)

Complexometric determination of iron and nickel: K. IZÁKOVÁ (12 *January* 1968)

Determination of lanthanum by flame photometric titration: G. SVEHLA and P. J. SLEVIN (15 *January* 1968)

A new volumetric method for estimation of fluorine: B. C. SINHA and S. K. ROY (15 *January* 1968)

Inorganic polarography in organic solvents—IV. The polarographic characteristics of metal-oxinate complexes in various solvents: R. M. DAGNALL and S. K. HASANNUDDIN (16 *January* 1968)

Solvent extraction of cobalt (II & III), nickel(II), palladium(II) and platinum(IV) with thenoyltrifluoroacetone: ANIL K. DE and CHITTARANJAN SAHU (16 *January* 1968)

Determination of scandium by atomic absorption: OWEN H. KRIEGE and G. G. WELCHER (17 *January* 1968)

Thin-layer chromatographic separation of scandium, yttrium, the rare earths, thorium and uranium(VI): KOICHI OGUMA (17 *January* 1968)

Talanta, 1968, Vol. 15, pp. i to ii. Pergamon Press. Printed in Northern Ireland

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Radiochemische Trennungen mit Hilfe der Ringofenmethode—III. Die Systeme ^{90}Sr/^{90}Y und ^{140}Ba/^{140}La: D. Klockow (17 *October* 1967)

New chromogens of the ferroin-type—I. Substituted triazines related to 6-cyano-2,2′-bipyridine: A. A. Schilt and K. R. Kluge (23 *October* 1967)

Untersuchungen an Reagenzien für Niob und Tantal—III. Die Reaktionen der Dibromgallussäure mit Niob(V) und Tantal(V): G. Ackermann and S. Koch (7 November 1967)

Studies with dithizone—XII. The formation of thiadiazolines by condensation with aldehydes and ketones: H. M. N. H. Irving and U. S. Mahnot (17 *November* 1967)

Investigation into the use of platinum ware for silicate analysis: B. G. Russell, Judy D. Spangenberg and T. W. Steele (17 *November* 1967)

Untersuchung der Reinheit metallochromer Indikatoren und photometrischer Reagenzien mittels chromatographischer Verfahren—I. Papierchromatographische Untersuchung von Azoderivaten der Chromotropsäure: J. Siemroth and I. Hennig (21 *November* 1967)

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Spectrophotometricextractive titrations—V. Theoretical approach to titration of a single cation: AFTANAS GALÍK (13 *December* 1967)

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SUMMARIES FOR CARD INDEXES

Determination of trace amounts of scandium by atomic absorption spectroscopy: Yiu-Kee Chau, *Talanta*, 1968, **15**, 421 (Department of Chemistry, Chung Chi College, The Chinese University of Hong Kong, Hong Kong.)

Summary—Optimum instrumental conditions were investigated for the determination of trace quantities of scandium by atomic-absorption spectroscopy. Enhancement effects by organic solvents and by complex extractions were also studied. ^{46}Sc was used to establish the optimum extraction conditions. A sensitivity of 0.06 ppm of Sc was observed when using extraction into oxine–butanol and atomic absorption was measured with an acetylene–nitrous oxide flame.

Separation and identification of some naturally occurring alkylphenanthrenes: Rolf Jönsson, *Talanta*, 1968, **15**, 425 (Department of Analytical Chemistry, University of Lund, Lund, Sweden.)

Summary—Different separation methods, especially gas chromatography, were applied to crude retene obtained from pine-wood tar. The relative retention times on three different columns, and the melting points, were used to identify the following compounds besides retene itself: 1-methylphenanthrene, 2-ethylphenanthrene, 1,7-dimethylphenanthrene, 1-methyl-7-ethylphenanthrene, 9,10-dihydroretene and possibly 1,3-dimethyl-7-ethylphenanthrene, 1,3-dimethyl-7-isopropylphenanthrene. All the substances formed aerosols at the outlet of the gas chromatograph. Superfine glass wool was found to be an excellent means of coagulating these aerosols.

Replacement substoichiometry and its application in activation analysis: Ivan Obrusník and Arnold Adámek, *Talanta*, 1968, **15**, 433 (Institute of Nuclear Research of Czechoslovak Academy of Sciences, Řež near Prague, Czechoslovakia.)

Summary—A new method based on the substoichiometry principle has been developed. Instead of substoichiometric amounts of chelating agent, substoichiometric amounts of aqueous solution of a competing metal are used. Theoretical relationships have been derived for this method of substoichiometric replacement. Possibilities for its application are discussed.

ОПРЕДЕЛЕНИЕ СЛЕДОВЫХ КОЛИЧЕСТВ СКАНДИЯ МЕТОДОМ АТОМНОАБСОРБЦИОННОЙ СПЕКТРОСКОПИИ:

YIU-KEE CHAU, *Talanta*, 1968, **15**, 421.

Резюме—Исследованы оптимальные условия аппаратуры для определения следовых количеств скандия методом атомно-абсорбционной спектроскопии. Также изучено влияние органических растворителей и извлечения в форме комплексов. Обнаружена чувствительность 0,06 мг/л в случае извлечения скандия раствором оксина в бутиловом спирте; атомная абсорбция измерена в пламени ацетилен– закись азота.

ВЫДЕЛЕНИЕ И ИДЕНТИФИКАЦИЯ НЕКОТОРЫХ ВСТРЕЧАЮЩИХСЯ В ПРИРОДЕ АЛКИЛФЕНАНТРЕНОВ:

ROLF JÖNSSON, *Talanta*, 1968, **15**, 425.

Резюме—Различные методы разделения, особенно газовая хроматография использованы в случае сырого ретена, полученного из паровой смолы. На основании относительных времён удерживания на трёх различных колонках и точк плавления идентифицированы следующие соединения кроме самого ретена: 1-метилфенантрен, 2-этилфенантрен, 1,7-диметилфенантрен, 1-метил-7-этилфенантрен, 9,10-дигидроретен и может быть 1,3-диметил-7-этилфенантрен, 1,3-диметил-7-изопропилфенантрен. Все вещества образовали аэрозоли на выходе из газового хроматографа. Отличным средством для коагуляции аэрозолей является очень тонкая стеклянная вата.

МЕТОД ЗАМЕЩАЮЩЕЙ СУБСТЕХИОМЕТРИИ И ЕГО ИСПОЛЬЗОВАНИЕ В АКТИВАЦИОННОМ АНАЛИЗЕ:

IVAN OBRUSNÍK and ARNOLD ADÁMEK, *Talanta*, 1968, **15**, 433.

Резюме—Разработан новый метод основывающийся на принципе субстехиометрии. Вместо субстехиометрических количеств хелирующего агента пользуются субстехиометрическими количествами водного раствора конкурирующего металла. Установлены теоретические отношения для этого метода замещающей субстехиометрии. Обсуждены возможности его применения.

Spectroscopy in separated flames—III. Use of the separated nitrous oxide-acetylene flame in thermal emission spectroscopy: G. F. Kirkbright, A. Semb and T. S. West, *Talanta*, 1968, **15**, 441 (Chemistry Department, Imperial College, London, S.W.7, U.K.)

Summary—The separation of a premixed nitrous oxide-acetylene flame at a modified commercial burner is described. The reducing interconal zone of the fuel-rich separated flame exhibits low radiative background. The reducing atmosphere and high temperature of this flame result in an effective medium for the excitation of the atomic line spectra of the refractory elements. The use of the fuel-rich flame in the flame photometry of these elements has been investigated.

Fluoreszenzanalytische Bestimmung von Sulfidionen im Nanogrammbereich: Adolf Grünert, Karlheinz Ballschmiter and Günther Tölg, *Talanta*, 1968, **15**, 451 (Institut für Anorganische Chemie und Kernchemie der Johannes Gutenberg-Universität, Mainz, Bundesrepublik Deutschland.)

Summary—The determination of sulphide in the range 1–10 ng/ml based on the quenching of the fluorescence of fluorescein-mercuric acetate in alkaline solution is described. Solutions of diphenylthiourea were used as calibration standards. The standard deviation was 0·17 ng/ml for 3·5 ng of sulphide per ml.

Studies on imidazole derivatives as chelating agents—V. Investigations of the applicabilities of the azoimidazoles as metallochromic indicators: Osamu Yamauchi, Hisashi Tanaka and Toyozo Uno, *Talanta*, 1968, **15**, 459 (Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto, Japan.)

Summary—Applicabilities of several azoimidazoles as metallochromic indicators were investigated in the light of the general equations expressing the colour change in the visual chelatometric titrations. By using the stability constants of the nickel(II), copper(II), zinc(II) and cadmium(II) chelates, the useful pH ranges, titration errors and sharpness of colour changes were predicted theoretically and the usefulness of these reagents as indicators was established experimentally. The Cu(II)–EDTA–indicator system was also examined experimentally. The OH-containing azoimidazoles could be applied to the direct titration of copper, nickel, zinc, cadmium, lead and bismuth and to the titration of calcium and cobalt in the presence of Cu(II)–EDTA. Attempts were made to construct diagrams for the estimation of titration errors and sharpness of colour changes.

СПЕКТРОСКОПИЯ В РАЗДЕЛЕННЫХ ПЛАМЕНАХ—III. ИСПОЛЬЗОВАНИЕ РАЗДЕЛЕННОГО ПЛАМЕНИ ЗАКИСИ АЗОТА И АЦЕТИЛЕНА В ТЕРМОЗМИССИОННОЙ СПЕКТРОСКОПИИ:

G. F. Kirkbright, A. Semb and T. S. West, *Talanta*, 1968, **15**, 441.

Резюме—Описано разделение предварительно смешанного пламени закиси азота и ацетилена в модифицированной коммерческой горелке. Восстанавливающая интерконусная зона богатого топливом разделенного пламени показывает низкий фон радиации. Восстанавливающая атмосфера и высокая температура этого пламени образуют действительную среду для возбуждения атомных линейних спектров огнеупорных элементов. Исследовано использование богатого топливом пламени в пламенной фотометрии этих элементов.

ОПРЕДЕЛЕНИЕ МЕТОДОМ ФЛУОРЕСЦЕНЦИИ НАНОГРАММОВЫХ КОЛИЧЕСТВ СУЛЬФИДИОНА:

Adolf Grünert, Karlheinz Ballschmiter and Günther Tölg, *Talanta*, 1968, **15**, 451.

Резюме—Описано определение сульфида в пределах 1–10 нг/мл, основывающееся на гашеифнилуоресценции флуоресцеина-ацетата ртути в щелочном растворе. Растворы дифенилтиомочевины использованы в качестве калибвовочных эталонов. Стандартная ошибка равна 0,17 нг/мл для 3,5 нг/мл сульфида.

ИЗУЧЕНИЕ ДЕРИВАТОВ ИМИДАЗОЛА В КАЧЕСТВЕ ХЕЛИРУЮЩИХ АГЕНТОВ—V. ИССЛЕДОВАНИЕ ПРИМЕНИМОСТИ АЗОИМИДАЗОЛОВ КАК МЕТАЛЛОХРОМНЫХ ИНДИКАТОРОВ

Osamu Yamauchi, Hisashi Tanaka and Toyozo Uno, *Talanta*, 1968, **15**, 459.

Резюме—Исследована применимость некоторых азоимидазолов в качестве металлохромных индикаторов на основании общих уравнений, описывающих перемену цвета в визуальных хелатометрических титрациях. Теоретически предсказаны ошибки титраций и резкость перемены цвета на основании констант устойчивости хелатов никеля(II), меди(II), цинка(II) и кадмия(II), и опытом установлена полезность этих реагентов в качестве индикатора. Также экспериментально испытана система Cu(II)-ЭДТА-индикатор. Содержащими OH-группу азоимидазолами можно пользоваться для прямого титрования меди, никеля, цинка, кадмия, свинца и висмута и для титрований кальция и кобальта в присутствии Cu(II)-ЭДТА. Покушалось сконструировать диаграммы для установления ошибок титрования и резкости перемены цвета.

New chromogens of the ferroin-type—I. Substituted triazines related to 6-cyano-2,2′-bipyridine: Alfred A. Schilt and Keith R. Kluge, *Talanta*, 1968, **15**, 475 (Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115, U.S.A.)

Summary—A spectrophotometric study has been made of the iron(II), cobalt(II), nickel(II) and copper(I) chelates of seven new compounds that contain the ferroin functional grouping. None of the new compounds proved to be superior to chromogenic reagents currently in use, but the results are of interest in designing new chromogens.

Improvement of iron determination by use of ferroin–organic dye ion-association complexes: M. Kníźek and M. Musilová, *Talanta*, 1968, **15**, 479 (A. S. Popov's Research Institute of Radiocommunications, Prague 4, Novodvorská 994, Czechoslovakia.)

Summary—Extraction of ion-associates of tris(1,10-phenanthroline)-iron(II) cation with monosulphonated azo dye anion into 1,2-dichloroethane is described. The method increases the sensitivity of the colorimetric determination of bivalent iron with 1,10-phenanthroline.

Application of 2-diphenylacetyl-1,3-indandione chemistry in the identification of organic compounds: W. A. Mosher, I. S. Bechara and E. J. Poziomek, *Talanta*, 1968, **15**, 482 (Department of Chemistry, University of Delaware, Newark, Delaware 19711, U.S.A.)

Summary—Derivatives of 2-diphenylacetyl-1,3-indandione have proved useful in identification of a wide variety of functional groups in organic compounds, and an account is given of their application in qualitative analysis.

НОВЫЕ ХРОМОГЕНЫ ТИПА ФЕРРОИНА—I. ЗАМЕЩЕННЫЕ ТРИАЗИНЫ СВЯЗАННЫЕ С 6-ЦИАНО-2,2′-БИПИРИДИНОМ:

Alfred A. Schilt and Keith R. Kluge, *Talanta*, 1968, **15**, 475.

Резюме—Изучены спектрофотометрическим методом хелаты железа(II), кобальта(II), никеля(II) и меди(I) семь новых соединений, содержащих функциональную группу ферроина. Ни одно от новых соединений не оказалося лучшим от хромогенных реагентов использованных в практике, но результаты интересные для синтеза новых хромогенов.

УЛУЧШЕННОЕ ОПРЕДЕЛЕНИЕ ЖЕЛЕЗА ИСПОЛЬЗОВАНИЕМ ИОНОАССОЦИАЦИОННЫХ КОМПЛЕКСОВ ФЕРРОИНА С ОРГАНИЧЕСКИМИ КРАСИТЕЛЯМИ:

M. Knížek and M. Musilová, *Talanta*, 1968, **15**, 479.

Резюме—Описано извлечение 1,2-дихлорэтаном ионоассоциационных комплексов трис(1,10-фенантролих)железо(II)-катиона с моносульфированным азокрасителем в качестве аниона. Этим методом повышается чувствительность колориметрического определения двувалентного железа 1,10-феннатролином.

ПРИМЕНЕНИЕ ХИМИИ 2-ДИФЕНИЛАЦЕТИЛ-1,3-ИНДАНДИОНА В ИДЕНТИФИКАЦИИ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ:

W. A. Mosher, I. S. Bechara and E. J. Poziomek, *Talanta*, 1968, **15**, 482.

Резюме—Производные 2-дифенилацетил-1,3-индандиона оказались полезным для идентификации ряда функциональных групп в органических соединениях; приведен обзор их использований в качественном анализе.

SUMMARIES FOR CARD INDEXES

Amplification reactions: R. Belcher, *Talanta*, 1968, **15**, 357 (Department of Chemistry, University of Birmingham, Birmingham 15, U.K.)

Summary—Amplification methods were first used over 100 years ago but the term only came into general usage during the development of microanalytical techniques. There has been a revived interest in amplification methods during the last few years, for it has been realized that by their application to trace analysis, it is often possible to obtain unusually precise results. The amplification methods available for various cations and anions are reviewed.

Improved method for the simultaneous absorptiometric determination of cobalt and nickel with quinoxaline-2,3-dithiol: J. A. W. Dalziel and A. K. Slawinski, *Talanta*, 1968, **15**, 367 (Department of Chemistry Chelsea College of Science and Technology, Manresa Road, London S.W.3.)

Summary—A new, more stable reagent, *S*-2-(3-mercaptoquinoxalinyl) thiuronium chloride (MQT), is proposed for the simultaneous absorptiometric determination of cobalt and nickel. It is hydrolysed rapidly to quinoxaline-2,3-dithiol (QDT) in ammonia buffer at pH 10. In the presence of zinc(II), QDT is stabilized by complex formation and the reagent blanks are reduced. Samples containing cobalt(II) and nickel(II) react with the mixture on warming to give 1:3 cobalt and 1:2 nickel complexes, with maximum absorbances at 472 and 520 mμ respectively. The sensitivity of the method is high, 0·0017 and 0·0029 $\mu g/cm^2$ for cobalt and nickel respectively, and there is a significant improvement in accuracy and precision, which is about $\pm 1\%$ over a 15-fold change in cobalt to nickel ratio. The selectivity is moderate; Ag(I), Cu(II), Pd(II), Cd(II), Hg(II), Sn(II), Pb(II), Bi(III) and Pt(IV) cause significant interference but most other common cations and anions can be tolerated.

АМПЛИФИКАЦИОННЫЕ РЕАКЦИИ:

R. Belcher, *Talanta*, 1968, **15**, 357.

Резюме—Амплификационные методы уже использованы перед 100 годов, но термин становился общепринятым только при развитии микроаналитических методов. За последние годы восстановлен интерес для амплификационных методов, понимая что, в их применении в следовом анализе, в многих случаях удалось получить замечательно точные результаты. Приведен обзор имеющихся амплификационных методов для ряда катионов и анионов.

УЛУЧШЕННЫЙ МЕТОД ОДНОВРЕМЕННОГО АБСОРБЦИОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ КОБАЛЬТА И НИКЕЛЯ ХИНОКСАЛИН-2,3-ДИТИОЛОМ:

J. A. W. Dalziel and A. K. Slawinski, *Talanta*, 1968, **15**, 367.

Резюме — *S*-2-(3-меркаптохиноксалинил) тиурониумхлорид (МХТ) предложен в качестве нового, более устойчивого реагента для одновременного абсорбциометрического определения кобальта и никеля. Реагент быстро гидролизируется в хиноксалин-2,3-дитиол (ХДТ) в аммиачном буферном растворе при pH 10. В присутствии цинка(II) ХДТ стабилизируется образованием комплекса, получая снижение фона реагента. Содержающие кобальт(II) и никель(II) пробы реагируют с смесью при загревании образуя 1:3 комплексы с кобальтом, а 1:2 комплексы с никелем, имеюшие максимумы светопоглощения при 472 и 520 ммк, соответсвенно. Метод обладает значительной чувствительностью—0,0017 мкг/см^2 для кобальта, а 0,0029 мкг/см^2 для никеля—и высокой точностью и воспроизводимостью—около 1 % в пределах 15 кратного отношения кобальт:никель. Избирательность метода умеренная: Ag(I), Cu(II), Pd(II), Cd(II), Hg(II), Sn(II), Pb(II), Bi(III) и Pt(IV) в значительной мере влияют на определение, но большинство других обыкновенных катионов могут терпеться.

Mass spectrometry of metal chelates—III. Further studies on metal oxinates: J. R. Majer, M. J. A. Reade and W. I. Stephen, *Talanta*, 1968, **15**, 373 (Department of Chemistry, University of Birmingham, P.O. Box 363, Edgbaston, Birmingham, 15, England.)

Summary—The mass spectra of the oxinates of gallium, dysprosium, beryllium, samarium, cadmium, neodymium, indium, bismuth, lanthanum, yttrium and gadolinium have been recorded. The results have been correlated with the structures proposed in the literature. The integrated ion current method has been applied to determine submicrogram quantities of some of these compounds. Oxinates insoluble in organic solvents or undergoing reaction on solution were precipitated directly in the evaporation probe. The factors which determine the suitability of metal chelates for the estimation of metals by this method are discussed together with the instrumental factors which determine the ultimate sensitivity.

Zur Polarographie der n-Butylzinnchloride: K. Issleib, H. Matschiner und S. Naumann, *Talanta*, 1968, **15**, 379 (Institut für Anorganische Chemie der Universität Halle, Saale, Deutsche Demokratische Republik.)

Summary—The determination of di-n-butyltin(IV) dichloride and tri-n-butyltin(IV) chloride in the presence of mono-n-butyltin(IV) trichloride with sodium diphenyldithiocarbamate by d.c. polarography is described. The investigations were made in solutions containing 5% of sodium acetate trihydrate in methanol, which dissolves the dithiocarbamates of the di-n-butyl and tri-n-butyl compounds and shifts the reduction wave of the mono-n-butyl compound to more negative potentials. Within certain limits the wave height is proportional to the concentration. In a mixture of the organotin chlorides, mono-n-butyltin trichloride is determined complexometrically. Tetrabutyltin is practically insoluble in methanol and does not interfere in the determinations.

Complexometric titration of calcium in the presence of larger amounts of magnesium: S. Tsunogai, M. Nishimura and S. Nakaya, *Talanta*, 1968, **15**, 385 (Department of Chemistry, Faculty of Fisheries, Hokkaido University, Hakodate, Japan.)

Summary—A simple and accurate titrimetric determination of calcium in the presence of larger amounts of magnesium is proposed. Calcium is extracted into a small volume of organic solvent as its glyoxal-bis(2-hydroxyanil) complex, and the calcium is titrated with EGTA. The end-point is sharp, and occurs when the red colour of the organic layer vanishes. This method has been successfully applied to the determination of calcium in sea-water with an error less than 0.1%.

МАСС-СПЕКТРОМЕТРИЯ ХЕЛАТОВ МЕТАЛЛОВ—III. ДАЛЬНЕЙШЕЕ ИЗУЧЕНИЕ ОКСИНАТОВ МЕТАЛЛОВ:

J. R. Majer, M. J. A. Reade and W. I. Stephen, *Talanta*, 1968, **15**, 373

Резюме—Получены масс-спектры оксинатов галлия, диспрозия, бериллия, самария, кадмия, неодима, индия, висмута, лантана, иттрия и гадолиния. Результаты сравнены с структурами предложенными в литературе. Использован метод интегрированного ионного тока для определения субмикрограммовых количеств некоторых из этих соединений. Оксинаты, нерастворимые в органических растворителях или реагирующие при растворении осаждали прямо в выпарном впуске. Обсуждаются факторы влияющие на применимость хелатов металлов в определении металлов этим методом, и инструментальные факторы определяющие предельную чувствительность.

ПОЛЯРОГРАФИЯ ХЛОРИДОВ Н-БУТИЛОЛОВА:

K. Issleib, H. Matschiner und S. Naumann, *Talanta*, 1968, **15**, 379.

Резюме—Описано определение ди-н-бутилолово(IV)дихлорида и три-н-бутилолово(IV)хлорида в присутствии моно-н-бутилолово(IV)трихлорида методом полярографии постоянным током с использованием дифенилдитиокарбамината натрия. Исследования провелось в растворах содержающих 5 % тригидрата ацетата натрия в метиловом спирте, который растворяет дитиокарбаминаты ди-н-бутил- и три-н-бутил-соединений и сдвигает волну восстановления моно-н-бутилсоединения к более отрицательному напряжению. В определённых пределах высота волны пропорциональна концентрации. В смеси хлоридов органоолова моно-н-бутил-оловотрихлорид определяли комплексонометрическим методом. Тетрабутил олово является практически нерастворимым в метиловом спирте и не влияет на определения.

КОМПЛЕКСОНОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КАЛЬЦИЯ В ПРИСУТСТВИИ БОЛЬШИХ КОЛИЧЕСТВ МАГНИЯ:

S. Tsunogai, M. Nishimura and S. Nakaya, *Talanta*, 1968, **15**, 385.

Резюме—Предложен несложный и точный метод титриметрического определения кальция в присутствии больших количеств магния. Кальций экстрагируют небольшим объемом органического растворителя в форме его комплекса с глиоксалбис(2-оксианилом) и титруют с ЭГТА. Острый конец титрования достигнут когда исчевает красная окраска органичесокого слоя. Методом успешно пользовались для определения кальция в морской воде с ошибкой меньше чем 0,1 %.

Polarographische Bestimmung des Schwefels in Benzin: H. Holzapfel und K. Schöne, *Talanta*, 1968, **15**, 391 (Institut für Anorganische Chemie der Karl-Marx-Universität, Leipzig, Deutsche Demokratische Republik.)

Summary—The polarographic determination of total sulphur, elemental sulphur, hydrogen sulphide, thiols, di- and polysulphides, thioethers and thiophenes in petrol is described. This method is applicable to the analysis of higher fractions, boiling below 250°. Besides the polarographic measurements, voltammetric determinations and amperometric titrations were carried out. After reduction to hydrogen sulphide, $10^{-4}\%$ total sulphur can be determined by voltammetric determination. The minimum determinable concentration of individual species is $10^{-3}\%$. Accuracies of 5% are achieved. An analytical scheme is included.

Polarographic microdetermination of halogens in organic compounds after oxygen flask combustion: G. M. Habashy, Y. A. Gawargious and B. N. Faltaoos, *Talanta*, 1968, **15**, 403 (National Research Centre, Dokki, Cairo, U.A.R.)

Summary—A method for the microdetermination of organic compounds containing halogens, by a polarographic finish, is reported. After the combustion of the organic sample in the oxygen flask, the products are absorbed in a suitable absorbent and chemically treated to produce Cl^-, Br^-, BrO_3^- or IO_3^- ions in solution before the polarography. The method is applicable to partially, highly, and fully halogenated aromatic and aliphatic compounds, whether solid or liquid. The results are generally within the acceptable limits of error.

Spot test for the detection of iodate in the presence of periodate. Application to the detection of *vic*-dihydroxy compounds: G. Nisli and A. Townshend, *Talanta*, 1968, **15**, 411 (Chemistry Department, The University, P.O. Box 363, Birmingham 15, U.K.)

Summary—Spot tests for the detection of 0·02 μg of iodate in the presence of 45 mg of periodate, and for the detection of 0·1 μg of *vic*-dihydroxy compounds are described. The tests are based on the iodide–iodate reaction, in the presence of periodate masked by an excess of molybdate.

ПОЛЯРОГРАФИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЕРЫ В БЕНЗИНЕ:

H. HOLZAPFEL und K. SCHÖNE, *Talanta*, 1968, **15**, 391.

Резюме—Описано полярографическое определение общей серы, элементарной серы, сероводорода, тиолов, ди- и полисульфидов, тиоэфиров и тиофенов в бензине. Метод применимый в анализе высших фракций, кипящих ниже 250°. Вместе с полярографическими измерениями проводились вольтамперометрические определения и амперометрические титрации. После восстановления в сероводород удалось определять $10^{-4}\%$ общей серы вольтамперометрическим методом. Минимальная определимая концентрация индивидуального типа соединения серы равна $10^{-3}\%$. Получены точности 5 %. Приведена схема анализа.

ПОЛЯРОГРАФИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ГАЛОГЕНОВ НА МИКРОШКАЛЕ В ОРГАНИЧЕСКИХ СОЕДИНЕНИЯХ ПОСЛЕ СОЖЖЕНИЯ В КОЛБЕ, НАПОЛНЕННОЙ КИСЛОРОДОМ:

G. M. HABASHY, Y. A. GAWARGIOUS and B. N. FALTAOOS, *Talanta*, 1968, **15**, 403.

Резюме—Описан микро-метод определения содержающих галогены органических соединений с использованием полярографического финиша. После сожжения органической пробы в колбе наполненной кислородом продукти абсорбируются в подходящем абсорбенте и обрабативаются химически для образования в растворе ионов Cl^-, Br^-, BrO_3^- или IO_3^- перед полярографическим определением. Методом можно пользоваться в анализе парциально, высоко или полно галогенированных ароматических или алифатических соединений, в жидом или твердом состоянии. В большинстве случаев результаты находятся в допустимых пределах ошибки.

КАПЕЛЬНАЯ ПРОБА ДЛЯ ОБНАРУЖЕНИЯ ИОДАТА В ПРИСУТСТВИИ ПЕРИОДАТА. ПРИМЕНЕНИЕ НА ОБНАРУЖЕНИЕ *vic*-ДИОКСИСОЕДИНЕНИЙ:

G. NISLI and A. TOWNSHEND, *Talanta*, 1968, **15**, 411.

Резюме—Описаны капельные пробы для обнаружения 0,02 мкг иодата в присутствии 45 мг периодата, и для обнаружения 0,1 мкг *vic*-диоксисоединений. Пробы основываются на реакции иодид-иодат, маскированной в присутствии периодата избытком молибдата.

Use of lanthanum and sulphuric acid to suppress interferences in the flame photometric determination of calcium in soil extracts: C. C. Evans and H. M. Grimshaw, *Talanta*, 1968, **15**, 413 (Merlewood Research Station, The Nature Conservancy, Grange-over-Sands, Lancashire, U.K.)

Summary—Interference by iron, aluminium and phosphate in the flame photometric determination of calcium in soil extracts is not fully suppressed by lanthanum unless dilute sulphuric acid is also present. The investigation was restricted to the oxy-acetylene flame.

The solubility of ^{14}C-labelled barium carbonate in aqueous systems: David P. Baccanari, Barbara A. Buckman, Marguerite M. Yevitz and Howard A. Swain Jr., *Talanta*, 1968, **15**, 416 (Wilkes College Chemistry Department, Wilkes-Barre, Pennsylvania 18703, U.S.A.)

Summary—The solubility of ^{14}C-labelled barium carbonate has been determined in basic aqueous solutions with and without added Ba^{2+} present and in aqueous solutions containing no added Ba^{2+} or OH^- ions. By use of activity coefficients from the literature, K_{SP} has been determined to be $4{\cdot}0 \times 10^{-10} \pm 0{\cdot}5 \times 10^{-10}$ at 25°.

Determination of sodium in high purity silica by activation analysis: B. T. Kenna and F. J. Conrad, *Talanta*, 1968, **15**, 418 (Sandia Laboratory, Analytical Methods Division 1121, Albuquerque, New Mexico 87115, U.S.A.)

Summary—High purity fused silica samples and NBS standards were irradiated in the Sandia Reactor Facility for 2 hr at a thermal flux of 10^{10} neutrons/cm^2/sec. ^{24}Na was produced by the reaction ^{23}Na(n, γ)^{24}Na (14·9 hr half-life, $\sigma = 0{\cdot}5$ barn), and decayed with emission of 1·37 and 2·75 MeV γ-rays. With the stated flux and irradiation time, sodium at the 3 ppm level has been determined with a standard deviation of 0·2 ppm. Values obtained by thermal neutron-activation analysis agree well with results obtained by emission spectrography and flame spectrophotometric methods.

ИСПОЛЬЗОВАНИЕ ЛАНТАНА И СЕРНОЙ КИСЛОТЫ ДЛЯ ПОДАВЛЕНИЯ ЭЛЕМЕНТОВ ВЛИЯЮЩИХ НА ОПРЕДЕЛЕНИЕ КАЛЬЦИЯ В ЭКСТРАКТАХ ПОЧВЫ МЕТОДОМ ПЛАМЕННОЙ ФОТОМЕТРИИ:

C. C. Evans and H. M. Grimshaw, *Talanta*, 1968, **15**, 413.

Резюме—Влияние железа, алюминия и фосфата на определение кальция в экстрактах почвы методом пламенной фотометрии не устранено полностью добавлением лантана если не присутствует разбавленная серная кислота. Исследование ограничивалось на пламя кислород- ацетилен.

РАСТВОРИМОСТЬ МЕЧЕННОГО С ^{14}C КАРБОНАТА БАРИЯ В ВОДНЫХ СИСТЕМАХ:

David P. Baccanari, Barbara A. Buckman, Marguerite M. Yevitz and Howard A. Swain Jr., *Talanta*, 1968, **15**, 416.

Резюме—Растворимость меченного с ^{14}C карбоната бария определена в основных водных растворах в присутствии и отсутствии избытка Ba^{2+} и в водных растворах не содержающих избыток ионов Ba^{2+} или OH^-. На основании коэффициентов активности опубликованных в литературе определен K_{sp} $4,0 \times 10^{-10} \pm 0,5 + 10^{-10}$ при 25°.

РАДИОАКТИВАЦИОННИЙ АНАЛИЗ: ОПРЕДЕЛЕНИЕ НАТРИЯ В ВЫСОКОЧИСТОТНОМ КРЕМНЕ:

B. T. Kenna and F. J. Conrad, *Talanta*, 1968, **15**, 418.

Резюме—Образцы высокочистотного плавленого кремня и эталоны NBS облучены в Сандия реакторе в течение 2 ч. при термическом флюксе 10^{10} нейтронов (см^2) сек. Образован ^{24}Na согласно реакции ^{23}Na(n, γ)^{24}Na (14,9 ч. полупериод, $\sigma = 0,5$ барн), который распадался с выпусканием гамма- лучей энергии 1,37 и 2,75 Мэв. Применяя упомянутый флюкс и время облучения определяли натрий при концентрации 3 мкг/г с стандартной ошибкой 0,2 мкг/г. Результаты полученные методом термического нейтронноактивационного анализа хорошо соглашаются с результатами полученными методами эмиссионной спектрографии и пламенной спектрофотометрии.

SUMMARIES FOR CARD INDEXES

The role of 70–80% perchloric acid as oxygen donor and the oxidation potentials made available: G. Frederick Smith, *Talanta*, 1968, **15**, 489 (Noyes Chemical Laboratories, University of Illinois, Urbana, Illinois, U.S.A.)

Summary—A study has been made of the probable oxidation potentials provided by perchloric acid in the concentration range 70–80%. The effect of acid concentration and temperature on the oxidation of chromium, vanadium, cerium, and manganese has been investigated. Available oxidation potentials appear to be 2.0–2.1 V or higher. The monohydrate of perchloric acid, $HClO_4 \cdot H_2O$, containing 84.6% of perchloric acid, has been made commercially available and authorized for distribution by common carrier. It can be diluted to give acid concentrations from 73.6% (corresponding to $HClO_4 \cdot 2H_2O$) upwards. Perchloric acid mixed with sulphuric acid is equivalent to high concentrations of perchloric acid and can be used for dissolution of ores and destruction of organic matter.

Isolation of osmium and ruthenium by ion-exchange paper and subsequent determination by X-ray fluorescence: H. Taylor and F. E. Beamish, *Talanta*, 1968, **15**, 497 (Department of Chemistry, University of Toronto, Toronto 5, Ontario, Canada.)

Summary—Quantitative separations of microgram quantities of osmium and ruthenium from large proportions of copper, iron and nickel were accomplished by the use of anion-exchange paper. Accurate determinations of osmium and ruthenium were made by adaptation of X-ray fluorescence. Wet methods for the dissolution of the paper and exchanger and subsequent wet determinations of osmium and ruthenium are discussed.

Metal chelate exchange in the organic phase—II. Extraction and exchange constants of dithizonates and diethyldithiocarbamates: Jiří Starý and Jaromír Růžička, *Talanta*, 1968, **15**, 505 (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Prague 1, Břehová 7, Czechoslovakia.)

Summary—Dithizonates and diethyldithiocarbamates of Ag, Tl(I), Cu(II), Zn, Cd, Hg(II), Pb, Fe(II), Co(II), Ni, Pd(II), In(III), As(III), Sb(III), Bi, Se(IV) and Te(IV) have been prepared and their reactions in carbon tetrachloride have been studied spectrophotometrically. From the exchange constants determined, the extraction constants of metal diethyldithiocarbamates have been calculated. Where formation of mixed chelates has been observed, corresponding exchange constants have been determined. Finally, the influence of organic solvents (CCl_4, $CHCl_3$, C_6H_6 and C_6H_5Cl) on the exchange reaction of zinc diethyldithiocarbamate with dithizone has been investigated.

РОЛЬ 70–80% ХЛОРНОЙ КИСЛОТЫ КАК ДАРИТЕЛЯ КИСЛОРОДА И ДОСТУПНЫЕ ПОТЕНЦИАЛЫ ОКИСЛЕНИЯ:

G. Frederick Smith, *Talanta*, 1968, **15**, 489.

Резюме—Изучены возможные потенциалы окисления, получаемые хлорной кислотой в пределах концентрации 70–80%. Исследовано влияние концентрации кислоты и температуры на окисление хрома, ванадия, церия и марганца. Доступные потенциалы окисления оказываются 2,0–2,1 в или выше. Моногидрат хлорной кислоты, $HClO_4 \cdot H_2O$, содержащий 84,6% хлорной кислоты, доступный торговле а также одобрено его распределение нормальным перевозом. Ее можно разбавлять чтобы получить концентрации 73,6% (соответствует $HCl_4O \cdot 2H_2O$) и выше. Смесь хлорной и серной кислот ответствует высоким концентрациям хлорной кислоты и ей можно пользоваться для растворения руд и разорения органических веществ.

ВЫДЕЛЕНИЕ ОСМИЯ И РУТЕНИЯ НА ИОНООБМЕННОЙ БУМАГЕ ИИХ ПОСЛЕДОВАТЕЛЬНОЕ ОПРЕДЕЛЕНИЕ МЕТОДОМ РЕНТГЕНОВСКОГО ФЛУОРЕСЦЕНТНОГО АНАЛИЗА:

H. Taylor and F. E. Beamish, *Talanta*, 1968, **15**, 497.

Резюме—Количественное отделение микрограммовых количеств осмия и рутения от больших количеств меди, железа и никеля получено использованием анионообменной бумагы. Точные определения осмия и рутения проведены методом рентгеновского флуоресцентного анализа. Обсуждены методы для растворения бумагы и ионообменныка и последовательного определения осмия и рутения мокрым путем.

ОБМЕН ХЕЛАТОВ МЕТАЛЛОВ В ОРГАНИЧЕСКОЙ ФАЗЕ—II. КОНСТАНТЫ ЭКСТРАКЦИИ И ОБМЕНА ДИТИЗОНАТОВ И ДИЭТИЛДИТИОКАРБАМИНАТОВ:

Jiří Starý and Jaromír Růžička, *Talanta*, 1968, **15**, 505.

Резюме—Приготовлены дитизонаты и диэтилдитиокарбаминаты Ag, Tl(I), Cu(II), Zn, Cd, Hg(II), Pb, Fe(II), Co(II), Ni, Pd(II), In(III), As(III), Sb(III), Bi, Se(IV) и Te(IV) и изучены их реакции в тетрахлорметане спектрофотометрическим методом. На основе определенных констант обмена вычислены константы экстракции диэтилдитиокарбаминатов металлов. В случае образования смешанных хелатов определены соответсвующие константы обмена. Конечно, исследовано влияние органических растворителей (CCl_4, $CHCl_3$, C_6H_6 и C_6H_5Cl) на реакцию обмена диэтилдитиокарбамината цинка с дитизоном.

Metal ion separations using cellulose phosphate as an ion-exchanger: DONALD H. SCHMITT and JAMES S. FRITZ, *Talanta*, 1968, **15**, 515 (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.)

Summary—Cellulose phosphate is used as a chelating ion-exchanger to effect the separation of several metal ions. Its exchange rate is much more rapid than that of a chelating ion-exchanger containing phosphonic acid groups on a polystyrene matrix. Weight distribution coefficients as a function of hydrogen ion concentration on cellulose phosphate are given for several metal ions. Successful separations of rare earths and alkaline earths, alkaline earths and alkali metals and aluminium and alkaline earths have been achieved on cellulose phosphate columns.

Spectrophotometric study of the reaction of iron(III) with Methylthymol Blue: BORISLAV KARADAKOV, DONKA KANTCHEVA and PETRANA NENOVA, *Talanta*, 1968, **15**, 525 (Department of Analytical Chemistry, Higher Institute of Chemical Technology and Metallurgy, Darvenitza, Sofia, Bulgaria.)

Summary—The reaction between iron(III) and Methylthymol Blue (MTB or H_6A) has been investigated by spectrophotometry. It has been established that iron(III) and MTB form two complexes with compositions iron(III): MTB = 1:1 and 1:2. The 1:1 complex is stable in acidic medium containing excess of iron, and the 1:2 complex is stable in slightly acidic or alkaline media containing excess of MTB. The absorption maxima are at 610 mμ (1:1) and 515 mμ (1:2), the molar absorptivities being $1{\cdot}73 \pm 0{\cdot}01 \times 10^4$ and $3{\cdot}21 \pm 0{\cdot}05 \times 10^3$ respectively. The nature of the two complexes at pH 6 and the stability constants have been determined: $\log \beta_{11} = 20{\cdot}56 \pm 0{\cdot}07$, $\log \beta_{112} = 43{\cdot}29 \pm 0{\cdot}09$, $\log \beta_{12} = 6{\cdot}66 \pm 0{\cdot}05$.

Catalytic microdetermination of chromium(VI): T. P. HADJIIOANNOU, *Talanta*, 1968, **15**, 535 (Laboratory of Analytical Chemistry, University of Athens, Athens, Greece.)

Summary—An automatic spectrophotometric kinetic method for the microdetermination of chromium(VI) is described, based on catalysis of the hydrogen peroxide–iodide reaction. The time required for the reaction to produce a small fixed amount of tri-iodide is measured automatically, and is proportional to the chromium(VI) concentration. Maximum tolerable amounts of various interfering ions were investigated. From 0·6 to 3·0 μg of chromium(VI) can be determined with relative errors of 1–2%, with measuring times of 10–50 sec.

РАЗДЕЛЕНИЕ ИОНОВ МЕТАЛЛОВ С ИСПОЛЬЗОВАНИЕМ ФОСФАТА ЦЕЛЛЮЛОЗЫ В КАЧЕСТВЕ ИОНООБМЕННИКА:

Donald H. Schmitt and James S. Fritz, *Talanta*, 1968, **15**, 515.

Резюме—Фосфатом целлюлозы пользовались в качестве хелирующего ионообменника для разделения некоторых ионов металлов. Скорость обмена значительно быстрее чем в случае хелирующего ионообменника, содержащего группы фосфокислоты на матрице полистирола. Приведены весовые коэффициенты распределения на фосфате целлюлозы дла некоторых ионов металлов в зависимости от концентрации водородных ионов. Получены успешные разделения редкоземельных элементов и щёлочноземельных элементов, щёлочноземельных элементов и щёлочных металлов и алюминия и щелочноземельных элементов на колонках фосфата целлюлы.

ИЗУЧЕНИЕ СПЕКТРОФОТОМЕТРИЧЕСКИМ МЕТОДОМ РЕАКЦИИ ЖЕЛЕЗА(III) С МЕТИЛТИМОЛОВЫМ СИНИМ:

Borislav Karadakov, Donka Kantcheva and Petrana Nenova, *Talanta*, 1968, **15**, 525.

Резюме—Исследована спектрофотометрическим методом реакция железа(III) и метилтимолового голубого МТС или H_6A). Установлено что железо(III) образует с МТС два комплекса в отношении железо(III): МТС = 1:1 и 1:2. Комплекс 1:1 является устойчивым в кислых средах содержащих избыток железа, а комплекс 1:2 устойчивый в слабокислых или щелочных средах содержающих избыток МТС. Максимумы светопоглощения находятся при 610 ммк (1:1) и 515 ммк (1:2), а молярные поглощения равны $1{,}73 \pm 0{,}01 \times 10^4$ и $3{,}21 \pm 0{,}05 \pm 10^3$, соответсвенно. Определены характеристики комплексов при pH 6 и их константы устойчивости: $\log \beta_{12} = 20{,}56 \pm 0{,}07$, $\log \beta_{112} = 43{,}29 \pm 0{,}09$, а $\log \beta_{12} = 6{,}66 \pm 0{,}05$.

МИКРООПРЕДЕЛЕНИЕ ХРОМА(VI) КАТАЛИТИЧЕСКИМ МЕТОДОМ:

T. P. Hadjioannou, *Talanta*, 1968, **15**, 535.

Резюме—Описан автоматический спектрофотометрический кинетический метод микроопределения хрома(VI), основывающийся на катализе реакции перекиси водорода с иодом. Автоматически определено время потребно для образования небольшего количества трииодида этой реакцией; это время пропорционально концентрации хрома(VI). Определены максимальные терпимые количества различных мешающих ионов. Этим методом определено 0,6 до 3,0 мкг хрома(IV), с относительной ошибкой 1–2%, а временем измерения 10–50 сек.

Radiochemische Trennungen mit Hilfe der Ringofenmethode—III. Die Systeme ^{90}Sr/^{90}Y und ^{140}Ba/^{140}La: D. Klockow, *Talanta*, 1968, **15**, 541 (Chemisches Laboratorium der Universität Freiburg i. Br., Analytische Abteilung, Bundesrepublik Deutschland.)

Summary—Rapid separations of ^{90}Y from ^{90}Sr and of ^{140}La from ^{140}Ba on carboxymethylcellulose filter papers by the ring-oven technique are described. Highest yields ($> 99\%$ for ^{90}Y and 90% for ^{140}La) and decontamination factors ($5 \times 10^3 - 10^4$ for ^{90}Y and 10^3 for ^{140}La) are obtained by using EDTA as complexing agent and water for washing. The half-lives of the daughter-nuclides were found to be $64{\cdot}7 \pm 0{\cdot}3$ hr and $40{\cdot}5 \pm 0{\cdot}2$ hr for ^{90}Y and for ^{140}La respectively. ^{90}Y can be selectively separated with 85–90% efficiency from a mixture of all four nuclides using a 1% solution of hydroxyisobutyric acid at pH 4·8 as eluent.

Simple and rapid determination of mercury in urine and tissues by isotope exchange: T. W. Clarkson and M. R. Greenwood, *Talanta*, 1968, **15**, 547 (Department of Radiation Biology and Biophysics, Atomic Energy Project, University of Rochester School of Medicine and Dentistry, Rochester, New York 14620, U.S.A.)

Summary—The method eliminates oxidation of organic material. Tracer quantities of ^{203}Hg are added to the sample and equilibrated with the stable mercury. ^{200}Hg vapor in nitrogen is passed through the sample in the presence of cysteine and at pH 7.4, and exchanges with the ^{203}Hg. The vapor is collected in a tube of activated Hopcalite placed in a gamma-counter. The increasing activity is recorded and the half-time of exchange is directly proportional to the mercury concentration in the sample. The method is best suited for urine samples containing more than 10 μg Hg/l.

Adsorption of chloro-complexes of the first row transition elements by Dowex A-1: D. G. Birney, W. E. Blake, P. R. Meldrum and M. E. Peach, *Talanta*, 1968, **15**, 557 (Department of Chemistry, University of Technology, Loughborough, U.K.)

Summary—A study has been made of the adsorption of chloro-complexes of the first row transition metals by the chelating resin Dowex A-1, and possible mechanisms for adsorption have been reviewed. Relative adsorption follows the series Zn(II) > Co(II) = Fe(III) $\gg$ Cu(II) > Mn(II). Negligible adsorption occurred with Cr(III) and none with V(IV) and Ni(II). Maximum adsorption of Zn(II) occurred from $3M$ hydrochloric acid and for the other metals from $8M$ acid.

РАДИОХИМИЧЕСКИЕ РАЗДЕЛЕНИЯ ПОМОЦЬЮ МЕТОДА КОЛЬЦЕВОЙ ПЕЧИ—III. СИСТЕМЫ ^{90}Sr/^{90}Y И ^{140}Ba/^{140}La:

D. Klockow, *Talanta*, 1968, **15**, 541.

Резюме—Описано быстрое разделение ^{90}Y от ^{90}Sr и ^{140}La от ^{140}Ba на фильтровальной бумаге из карбоксиметилцеллюлозы методом кольцевой печи. Найлучшие выходы для (> 99% для ^{90}Y и 90% для ^{140}La) и факторы деконтаминации (5 × 10^3–10^4 для ^{90}Y и 10^3 для ^{140}La) получены использованием ЭДТА в качестве комплексообразующего агента и води для промывки. Период полураспада дочерных нуклидов равны 64,7 ± 0,3 ч. и 40,5 ± 0,2 ч. для ^{90}Y и для ^{140}La, соответственно. ^{90}Y можно выделят селективно с выходом 85–90 % из смеси всех четырех нуклидов пользуясь 1 %-тным раствором оксиизомасляной кислоты в качестве элюента при pH 4,8.

НЕСЛОЖНОЕ И БЫСТРОЕ ОПРЕДЕЛЕНИЕ РТУТИ В МОЧЕ И ТКАНЯХ МЕТОДОМ ОБМЕНА ИЗОТОПОВ:

T. W. Clarkson and M. R. Greenwood, *Talanta*, 1968, **15**, 547.

Резюме—Метод исключает окисление органического вещества. Пробы добавляют индикаторные количества ^{203}Hg и уравновешивают с устойчивой ртутью. Пары ^{200}Hg в азоте пропускают через раствор пробы в присутствии цистеина при pH 7,4 и обменяют с ^{203}Hg. Пары собирают в трубке из активированного нопкалита, смещенной в гамма-счётчике. Записано повышение активности, а полупериод обмена пропорционален концентрации ртути в пробе. Метод очень полезный для анализа проб мочы содержащих больше чем 10 мкг/л Hg.

АДСОРБЦИЯ ХЛОРКОМПЛЕКСОВ ПЕРЕХОДНЫХ ЭЛЕМЕНТОВ ПЕРВОГО РЯДА НА СМОЛЕ ДАУЕКС А-I

D. G. Birney, W. E. Blake, P. R. Meldrum and M. E. Peach, *Talanta*, 1968, **15**, 557.

Резюме—Изучена адсорбция хлоркомплексов переходных элементов первого ряда на хелатообразующей смоле Дауекс А-I, и обсуждены возможные механизмы этой адсорбции. Относительная адсорбция следует ряду Zn(II) > Co(II) = Fe(III) ≫ Cu(II) > Mn(II). Cr(III) адсорбировался в незначительной мере, а V(IV) и Ni(II) не адсорбировались. Максимальная адсорбция Zn(II) обнаружена из $3M$ соляной кислоты, а остальных металлов—из $8M$ кислоты.

Micro and semi-micro determination of organic nitrogen by use of potassium bromate: Mohammad Ashraf, M. A. Siddiqui and M. K. Bhatty, *Talanta*, 1968, **15**, 559 (West Regional Laboratories, C.S.I.R., Lahore, Pakistan.)

Summary—After Kjeldahl digestion of an organic compound, nitrogen is determined by oxidation of the resultant ammonium sulphate with hypobromite produced *in situ* by the addition of an excess of potassium bromate and bromide in a special flask. The unreacted potassium bromate is determined iodometrically.

The 1:3 uranium(VI)–8-hydroxyquinoline compound: its composition and thermal conversion into bis(8-hydroxyquinolinato)dioxouranium(VI) A. Corsini and J. Abraham, *Talanta*, 1968, **15**, 562 (Department of Chemistry, McMaster University, Hamilton, Ontario, Canada.)

Summary—Evidence is provided to show that in the red compound formed between uranium(VI) and 8-hydroxyquinoline, the ligand-to-uranium ratio is slightly lower than 3:1, at least when the compound is prepared by a widely accepted procedure. Competition between 8-hydroxyquinoline and other ligands such as water or ammonia is probably responsible for the non-stoichiometry. Further, it is shown that a procedure frequently used for the thermal conversion of the red compound into bis(8-hydroxyquinolinato)dioxouranium(VI) yields a compound in which the ligand-to-uranium ratio is less than 2:1. Conditions which lead to the thermal preparation of the stoichiometric bis compound are described.

Application of electroluminescence techniques to the determination of aromatic hydrocarbons: B. Fleet, G. F. Kirkbright and C. J. Pickford, *Talanta*, 1968, **15**, 566 (Chemistry Department, Imperial College, London, S.W.7.)

Summary—An account is given of the quantitative determination of certain fused-ring aromatic hydrocarbons by means of the electroluminescence induced by application of a small a.c. voltage to inert electrodes placed in a solution of the hydrocarbon in dimethylformamide.

МИКРО-И СЕМИМИКРОМЕТОД ОПРЕДЕЛЕНИЯ ОРГАНИЧЕСКОГО АЗОТА С ИСПОЛЬЗОВАНИЕМ БРОМАТА КАЛИЯ:

Mohammad Ashraf, M. A. Siddiqui and M. K. Bhatty, *Talanta*, 1968, **15**, 559.

Резюме—После дигерирования органического соединения методом Кьельдаля азот определяют окислением образованного сульфата аммония произведенным *in situ* гипобромитом; он получается добавлением раствору избытка бромата и бромида калия в специальной колбе. Нереагированный бромат калия определяют иодометрическим методом.

СОЕДИНЕНИЕ УРАНА(VI) С 8-ОКСИХИНОЛИНОМ В ОТНОШЕНИИ 1:3:ЕГО СОСТАВ И КОНВЕРСИЯ В БИС(8-ОКСИХИНОЛИНАТО) ДИОКСИУРАН(VI):

A. Corsini and J. Abraham, *Talanta*, **1968, 15**, 562.

Резюме—Приведены экспериментальные данные показывающие что образованное из урана(VI) и 8-оксихинолина красное соединение имеет отношение лиганда к урану немного ниже чем 3:1, по крайней мере в случае приготовления соединения следуя широко принятую процедуру. Нестехиометрическое отношение можно считать результатом соревнования между лигандами, такими как вода или аммиак. Кроме того показано что часто использованная процедура для термической конверсии красного соединения в бис(8-оксихинолинато) диоксиуран(VI) дает соединение имеющее отношение лиганда к урану меньше чем 2:1. Описаны условия для приготовления стохиометрического бис-соединения термческим путем.

ПРИМЕНИЕ МЕТОДОБ ЭЛЕКТРОЛЮМИНЕСЦЕНЦИН В ОНРЕЛЕЛЕНИИ АРОМАТИЧЕСКИХ ЛГЛЕВОЛОРОЛОВ:

B. Fleet, G. F. Kirkbright and C. J. Pickford, *Talanta*, 1968, **15**, 566.

Резюме—Рассмотрено количественное определение некоторых ароматических углеводородов имеющих конденсированные ядра методом электролюминесценции, вызванной прикладыванием небольшего потенциала переменного тока к инертными электродами, помещенными в раствор углеводорода в диметилформамиде.

Spectrofluorimetric determination of microgram amounts of lead: G. F. Kirkbright and C. G. Saw, *Talanta*, 1968, **15**, 570 (Chemistry Department, Imperial College, London, S.W.7.)

Summary—The violet fluorescence at 480 mμ of lead in concentrated hydrochloric acid–potassium chloride solution (excitation maximum 270 mμ) provides a method for the spectrofluorimetric determination of 10–60 μg of lead. The optimum conditions for the determination have been established, and the effect of 31 foreign ions examined at the 50-fold molar excess level. The interference from iron(III) and vanadium(V) is eliminated by addition of tin(II) chloride, and that of chromium(VI) by treatment with sodium sulphite.

Determination of copper in geological material by neutron activation and gamma-gamma coincidence spectrometry: O. B. Michelsen and E. Steinnes, *Talanta*, 1968, **15**, 574 (Institutt for Atomenergi, Kjeller, Norway.)

Summary—The copper content of some geological samples has been determined by thermal neutron activation and subsequent coincidence gamma-spectrometry, taking advantage of the 180° annihilation quanta of ^{64}Cu. By this means the interference of ^{24}Na, which is often the major gamma-activity induced in geological materials, is greatly reduced. The method is precise to about $\pm 5\%$, and the error is of the same order. The method should be especially attractive for application to samples with a copper content of 100–1000 ppm.

Kinetic titration with differential thermometric determination of the end-point: I. Sajó, *Talanta*, 1968, **15**, 578 (Iron and Steel Research Institute, Budapest, Hungary.)

Summary—A method has been described for the determination of concentrations below $10^{-4}M$ by applying catalytic reactions and using thermometric end-point determination. A reference solution, identical with the sample solution except for catalyst, is titrated with catalyst solution until the rates of reaction become the same, as shown by a null deflection on a galvanometer connected *via* bridge circuits to two opposed thermistors placed in the solutions.

СПЕКТРОФЛУОРОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МИКРОГРАММОВЫХ КОЛИЧЕСТВ СВИНЦА:

G. F. Kirkbright and C. G. Saw, *Talanta*, 1968, **15**, 570.

Резюме—Фиолетовая флуоресценция свинца в растворе концентрированной соляной кислоты и хлорида калия при 480 ммк (максимум возбуждения 270 ммк) составляет основу метода для спектрофлуорометрического определения свинца в пределах 10–60 мкг. Определены оптимальные условия определения и изучено влияние 31 посторонных ионов в 50-кратном молярном избытке. Влияние железа(III) и ванадия(V) исключено добавкой хлорида олова(II), а влияние хрома(VI)—обработкой сульфитом натрия.

ОПРЕДЕЛЕНИЕ МЕДИ В ГЕОЛОГИЧЕСКИХ ВЕЩЕСТВАХ МЕТОДАМИ НЕЙТРОННОЙ АКТИВАЦИИ И СПЕКТРОМЕТРИИ ГАММА-ГАММА КОИНЦИДЕНЦИИ:

O. B. Michelsen and E. Steinnes, *Talanta*, 1968, **15**, 574.

Резюме—Содержание меди некоторых геологических образцев определено методом активации термическими нейтронами и последующей спектрометрии гамма-коинциденции, воспользоваясь квантами уничтожения при 180° ^{64}Cu. Этим образом снижено в значительной мере влияние ^{24}Na, являющееся часто главной гамма активности, индуцированной в геологических вещесвтах. Точность метода около 5%, а ошибка этой же величины. Метод является очень полезным для образцев, содержающих 100–1000 мкг/г меди.

КИНЕТИЧЕСКАЯ ТИТРАЦИЯ С ДИФФЕРЕНЦИАЛЬНЫМ ТЕРМОМЕТРИЧЕСКИМ ОПРЕДЕЛЕНИЕМ КОНЦА ТИТРОВАНИЯ:

I. Sajó, *Talanta*, 1968, **15**, 578.

Резюме—Описан метод для определения концентраций ниже чем $10^{-4}M$, пользуясь каталитическими реакциями и термометрическим определением конца титрования. Эталонный раствор, того же самого состава как раствор пробы кроме катализатора, титруют раствором катализатора до уравнения скоростей реакции, которое обнаруживают отклонением нуль на гальванометре, соединенном путем мостиковых цепей с двумя противоположными термисторами, помещенными в растворах.

Talanta, 1968, Vol. 15, p. ii. Pergamon Press. Printed in Northern Ireland

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Mass Spectrometry in Inorganic Chemistry: ROBERT F. GOULD. American Chemical Society, Washington, D.C., 1968, Pp. vii + 329. $12.

This is a report of a symposium on inorganic mass spectrometry sponsored by the Division of Inorganic Chemistry at the 152nd meeting of the American Chemical Society in 1966. The contents include 21 separate contributions which cover a very wide range of interest. Among the topics reported are chemi-ionization, high temperature studies, electron impact, and the analysis of complex volatile inorganic substances such as perfluorosilane.

Phosphorimetry: M. ZANDER, Academic Press, New York, 1968. Pp. viii + 206. 93s. 4d.

This is the first major publication to deal exclusively with phosphorimetry and should fulfill the needs of analysts, biochemists and workers in clinical chemistry. The first part contains an introduction to the theoretical and experimental foundations of phosphorescence anda comprehensive collection of phosphorescence characteristics for different compounds. The second part gives experimental procedures for spectrophosphorimetry and lists a large number of applications of the technique to many branches of chemistry. Examples of the fields covered are analysis of polycyclic aromatic hydrocarbons, coal-tar fractions and petroleum products, air pollution studies, determination of inhibitors in polymers, and applications in biochemistry, pharmacology and food chemistry. The conprehensive author and subject indexes make this an invaluable reference book for the research worker who wishes to use this powerful technique.

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Fluoreszenzanalytische Bestimmung von Sulfidionen im Bereich von 1–10 ng/ml: Adolf Grünert, Karlheinz Ballschmiter and Günther Tölg (10 *October* 1967)

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Automatic analysis with thermometric detection: W. R. McLean and G. E. Penketh. (26 *May* 1968)

Determination of the precise composition of the triple sodium uranyl acetates of magnesium, zinc and nickel and some observations on the use of the first two compounds for the determination of sodium: R. G. Monk. (26 *May* 1968)

Amperometric titration of thorium with copper(II) as amperometric indicator: J. R. Dean and W. E. Harris. (27 *May* 1968)

Electrodeless bismuth discharge tubes: R. M. DAGNALL, K. C. THOMPSON and T. S. WEST. (27 *May* 1968)

Determination of traces of perchlorate in chlorate solutions: D. L. FUHRMAN. (4 *June* 1968)

New chromogens of the ferroin type—IV. Pyridylpyrimidines and bidiazines: A. A. SCHILT. (5 *June* 1968)

Studies in atomic fluorescence spectroscopy—VIII. Atomic fluorescence and atomic absorption of thallium and mercury with electrodeless discharge tubes as sources: R. F. BROWNER, R. M. DAGNALL and T. S. WEST. (6 *June* 1968)

Metal complexes with tropolones: YAG DUTT, R. P. SINGH and MOHAN KATYAL. (7 *June* 1968)

Simultaneous spectrophotometric determination of traces of copper, nickel and cobalt: L. BALABANOFF and S. SELMAN. (15 *June* 1968)

***N*-Salicylidene-β-alanine as a gravimetric reagent for copper(II):** R. K. MEHTA, S. P. RAO and R. C. KAPOOR. (15 *June* 1968)

Spectrophotometric determination of antimony with 3,5,7,4′-tetrahydroxyflavone (Kaempferol): B. S. GARG, K. C. TRIKHA and R. P. SINGH. (17 *June* 1968)

Application of a demountable water-cooled hollow-cathode lamp to atomic-fluorescence spectrometry: G. ROSSI and N. OMENETTO. (17 *June* 1968)

Paper chromatographic separation of a few cations with t-butanol and ethanol mixture in acid: SUMAN SETHI and R. S. RAI. (17 *June* 1968)

Metal chelate exchange in the organic phase—III. Extraction and exchange constants of dithizonates and oxinates: JIŘÍ STARÝ. (17 *June* 1968)

Advantages of a two-detector system in automated substoichiometric radioisotope-dilution analysis: C. G. LAMM and J. RŮŽIČKA. (17 *June* 1968)

Colorimetric determination of cerium with Chromotrope 2B: I. I. M. ELBEIH and M. S. RISK. (17 *June* 1968)

Electron microscopy and diffraction studies on coprecipitation—II. Coprecipitation of barium and lead sulphates: KAZUYOSHI TAKIYAMA and EIKO KOZUKI. (19 *June* 1968)

Atomic-absorption spectrophotometry in water analysis: S. D. SOMAN, V. K. PANDAY and K. T. JOSEPH. (20 *June* 1968)

Talanta, 1968, Vol 15, p 111 Pergamon Press Printed in Northern Ireland

PUBLICATIONS RECEIVED

Progress in Nuclear Energy, Series IX, Analytical Chemistry, Vol. 8 Pt. 2: H A ELION and D C STEWART (Eds). Pergamon, Oxford, 1968 pp 86. £2

This part of Volume 8 consists entirely of a review by Chester J Schuler on laser-induced spontaneous and stimulated Raman scattering It is a model of review writing, concise, clear, interesting, packed with data and containing a well organized bibliography (up to mid-1967). The advent of the laser has clearly stimulated much activity in Raman spectroscopy and made the analytical potential of the method realizable Despite appearing in this series, the review is not aimed at analysts, but it is a good starting point for those wishing for background information on the impact of laser light sources in Raman spectroscopy, the advantages and problems associated with their use, and the nature of the stimulated Raman effect

Chimie Nucléaire Appliquée: E ROTH Masson et C^{ie}, Paris, 1968 pp ix + 629 98 F (French)

This is a comprehensive textbook dealing succinctly with all aspects of nuclear chemistry. After an introductory chapter which surveys the subject there is a lengthy chapter dealing with basic theory and concepts This is followed by chapters on the use of radioactive tracers in chemistry, mass spectrometry and the analysis of stable isotopes, isotope dilution, the Mossbauer effect and the properties of radioactive tracers There is also a series of chapters describing the artificial preparation of radioelements (including the transuranic elements), activation analysis, radiation chemistry, nuclear fission, dosimetry, and the practical applications of the interaction of matter and radiation There is a extensive bibliography and useful sets of tables of nuclear data. A valuable inclusion is a section with a number of set problems This book is recommended to third year students and research workers and to those engaged in teaching all aspects of nuclear chemistry

Comprehensive Analytical Chemistry, Vol. IIB, Physical Separation Methods: eds CECIL L WILSON and DAVID W WILSON with (the late) C R N STROUTS Elsevier, Amsterdam, 1968 pp xv + 445 £8 10

This volume, covering liquid chromatography in columns, gas chromatography, ion exchangers and distillation, continues the exposition of analytical chemistry in this well known series, and maintains the standards set

The Limit of Detection of a Complete Analytical Procedure: H KAISER and A C MENZIES Hilger, London, 1968 pp ix + 59 30s

This little book consists of a translation of two papers by Professor Kaiser on the limits of detection, and an introduction to statistics by Dr Menzies It is very readable and will be of use to all involved in trace analysis, and of interest to analysts in general.

Talanta, 1968. Vol. 15. p. iii. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Atomic-Absorption Spectroscopy and Analysis by Atomic-Absorption Flame Photometry: JUAN RAMÍREZ-MUÑOZ. Elsevier, Amsterdam, 1968. Pp. xii + 493. 195s.

This is a typically thorough Ramírez-Muñoz text, in the tradition of the classic text on flame photometry written by Burriel-Martí and Ramírez-Muñoz. There is a comprehensive account of the principles of the method, of the apparatus used, and of the methods available, and there is a very useful appendix which summarizes the conditions for determination of 68 elements. This volume is likely to prove an indespensible part of the flame spectroscopist's reference library.

Analytical Letters: Editors GEORGE G. GUILBAULT and LARRY G. HARGIS. Dekker, New York, 1967. £5. 7. 6 per volume.

This is a new venture in the publishing of analytical papers, designed to minimize the time of publication. It will appear monthly. Time is saved by photographic reproduction methods direct from the manuscript, placing a premium on accurate and clean preparation of the copy submitted. The future of this venture will be watched with interest.

Spectroscopy Letters: Editor JAMES W. ROBINSON. Dekker, New York, 1968. £5. 7. 6 per volume.

This is a companion journal to *Analytical Letters,* intended to provide a similar service of rapid publication in the field of spectroscopy.

Proceedings of the First International Conference on Forensic Activation Analysis: Editor V. P. GUINN. Gulf General Atomic, P.O. Box 608, San Diego, California 92112, 1967. Pp. ix + 314. $7.00.

A report of the conference held in San Diego in September 1966 containing the texts of the papers presented, this volume is a fascinating account of the forensic applications of activation analysis, showing the very wide range of investigation that the modern criminological chemist is required to undertake.

Talanta, 1968, Vol. 15, pp. iii to iv. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Electroanalytical Chemistry, Vol. 2: Ed. Allen J. Bard. Edward Arnold, London, 1967. Pp. 270. 105s.

This is the second volume in the series, and adds four authoritative and well written reviews in the field, on the topics "Electrochemistry of Aromatic Hydrocarbons and Related Substances", "Stripping Voltammetry", "The Anodic Film on Platinum Electrodes", and "Oscillographic Polarography at Controlled Alternating Current". Each review gives a comprehensive introduction with theoretical background, and a discussion of practical applications with a useful bibliography. The book will be of value to researchers and graduate students with an interest in electrochemical methods of analysis.

Handbuch der Analytischen Chemie—Quantitative Analyse, Band 1bβ—Silber und Gold: H. W. Haase. Springer Verlag, Berlin, 1967. Pp. 137 (Ag), +82 (Au), +51 (Fire assay methods and techniques). DM 74.00.

There can be very few problems in the determination of silver or gold which will not be solved or at least simplified by consultation of this book. The vast amount of detailed information is readily available through indexes and tables. Non-German speaking people need not be put off by the thought of language difficulties—the book is very clearly and concisely written. A useful feature is the separate chapter on fire assay methods applicable to both these metals and also to other noble metals. A valuable reference book for all engaged on analysis of noble metals.

Selected Readings in Chemical Kinetics: Ed. Margaret H. Back and Keith J. Laidler. Pergamon, Oxford, 1967. Pp. 175. Hard cover 30s ($5.50). Flexi-cover 20s ($4.00).

This book will fill a gap in many younger libraries, where runs of older journals are not available for consultation by students. The 12 papers have been carefully selected as being both milestones in the progress of reaction kinetics and at the present time a help to the student's understanding of the subject. Three papers are translated from the German, and one from Russian; perhaps the ones in German might have been left untranslated, as useful practice in reading in a foreign language. The price should fall within the pocket of most students.

Chelates in Analytical Chemistry, Vol. 1: Ed. H. A. Flaschka and A. J. Barnard, Jr. Edward Arnold, London, 1967. Pp. xii + 418. £7.10s.

This is the first volume of a series of authoritative reviews of the analytical applications of chelate compounds. The avowed object is to show that chelation is a unifying principle over a wide field of chemistry. The topics covered in this first volume (history, chromogenic agents, chelating resins, conductimetry, thermal dissociation, polarography, and molybdenum and tungsten chemistry) together with the list of distinguished contributors should serve as guarantee that the aim will be realized.

Basic Principles of Chemistry: Harry B. Gray and Gilbert P. Haight, Jr. Benjamin, New York, 1967. Pp. XVII + 595. $9.75.

A well-illustrated account of the modern outlook on chemistry and the way in which it should be taught, this book can confidently be recommended to first and second year students and those who wish to bring their chemistry up to date.

Modern Organic Chemistry: John D. Roberts and Marjorie C. Caserio. Benjamin, New York, 1967. Pp. xxi + 844. 86s.

This book certainly lives up to its title and presents organic chemistry in modern terms of bonding theory, thermodynamics, kinetics and reaction kinetics, so helping to get away from the traditional (and unfortunate) subdivisions of chemistry. The whole field of organic chemistry is covered and there is a refreshing lack of cataloguing of information. The extensive use of the results of the newer spectroscopic techniques is a particularly praiseworthy feature. For the teacher there is a companion volume "Supplement for Modern Organic Chemistry" (pp. 525; 325) which contains the answers to the problems, with further discussion where necessary.

Hormone Chemistry: W. R. Butt. Van Nostrand, London, 1967. Pp. xvi + 397. 75s.

Purification of Acetonitrile and Tests for Impurities: J. F. Coetzee. Butterworths, London, 1967. Pp. 7. 3s. (Reprint of *Pure and Applied Chemistry*, 1966, **13** (3), 429–435.)

Preparation of Anhydrous Ethylenediamine: L. M. Mukherjee and S. Bruckenstein. Butterworths, London, 1967. Pp. 6. 3s. (Reprint of *Pure and Applied Chemistry*, 1966, **13** (3), 421–426.)

NOTICES

U.S.A.

30 *June*–5 *July* 1968, **The First International CODATA Conference** on the critical evaluation of numerical property values in the physical sciences will be held at Arnoldshain in the Taunus Mountains near Frankfurt/Main from 30 June to 5 July 1968. This Conference will be under the auspices of the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions (ICSU). It will be run along the informal lines of the Gordon Conferences in the U.S.A. and the EUCHEM Conferences in Europe. The General Chairman of the Conference will be Prof. Dr. W. Klemm, Vice President of CODATA and recently president of IUPAC.

CODATA is a committee of ICSU started in 1966 to stimulate and coordinate informally on a world-wide basis the rapidly growing effort to collect, evaluate, compile and publish the evaluated numerical data of science and technology. Six major countries (France, Germany, Japan, U.K., U.S.A. and U.S.S.R.) and eleven International Unions of ICSU are represented on the committee.

Information and application forms to attend the meeting may be obtained from Dr. Guy Waddington, Executive Director, Central Office, CODATA, c/o National Academy of Sciences, 2101 Constitution Ave. N.W., Washington, D.C. 20418, U.S.A.

DEUTSCHE DEMOKRATISCHE REPUBLIK

18–20 *September* 1968, **Optische Spektralanalyse.** Das Institut für analytische Chemie der Technischen Hochschule für Chemie "Carl Schorlemmer" Leuna-Merseburg veranstalst vom 18–20 September 1968 eine Tagung zum Thema

"Optische Spektranalyse"

In Plenar- und Diskussionsvorträgen soll insbesondere die Bedeutung der Intensität als Stoffkonstante und als analytische Meßgröße in den verschiedenen Bereichen des optischen Spektrums behandelt werden. Dabei stehen im Vordergrund methodische Fortschritte und neuere theoretische Erkenntnisse der Atomspektroskopie (neue Anregungsquellen, Atomabsorption), der Molekülspektroskopie (IR- und UV-Spektroskopie) und auch allgemein interessierende, mit der Intensitätsmessung zusammenhängende metrologische Probleme.

Anmeldungen für Diskussionsvorträge (Zeit 20 min) werden mit kurzer Inhaltsangabe in doppelter Ausfertigung bis 1.3.1968 erbeten an

Institut für analytische Chemie
der Technischen Hochschule für Chemie
"Carl Schorlemmer" Leuna-Merseburg
42 *Merseburg* (DDR)
Geusaer Straße

Anmeldungen für die Teilnahme an dieser Tagung müssen bis 1.4.1968 vorliegen. Alle weiteren Einzelheiten (wissenschaftliches Programm, Damenprogramm, organisatorische. Bisher eingegangene Interessentenmeldungen gelten als Anmeldung und werden berücksichtigt.

SUMMARIES FOR CARD INDEXES

Spectroscopy in separated flames—IV. Application of the nitrogen-separated air–acetylene flame in flame-emission and atomic-fluorescence spectroscopy: R. S. HOBBS, G. F. KIRKBRIGHT, M. SARGENT and T. S. WEST, *Talanta*, 1968, **15**, 997 (Chemistry Department, Imperial College, London, S.W.7.)

Summary—The primary and secondary combination zones of an air–acetylene flame have been separated by a stream of nitrogen flowing parallel to the flame to prevent access of atmospheric oxygen to its base. The flame is very stable over a wide range of fuel–air mixture strengths, and organic solvents may be aspirated without difficulty. The low flame background enables thermal-emission and atomic-fluorescence measurements to be made with high sensitivity. Bismuth, for example, has been determined in the range 5–200 ppm by its thermal emission at 306·8 nm, with a detection limit of 2 ppm in aqueous solution, and in the range 1–10 ppm with a detection limit of 0.3 ppm in 50% ethanolic solution. Zinc and cadmium have been determined at 213·9 nm and 228·8 nm by atomic-fluorescence spectroscopy in this flame with detection limits of 2×10^{-4} ppm and 5×10^{-4} ppm respectively, vapour-discharge lamps being used as sources of excitation. The results obtained represent a considerable improvement over those available by the same methods in a conventional air–acetylene flame.

Evaluation of the lanthanum fluoride membrane electrode response in acidic solutions: The determination of the pK_a of hydrofluoric acid: NICHOLAS E. VANDERBORGH, *Talanta*, 1968, **15**, 1009 (Analytical Methods Division—5421, Sandia Laboratory, Albuquerque, New Mexico, U.S.A.)

Summary—Measurements made with a combination of glass and lanthanum fluoride membrane electrodes in solutions which are strongly acid but varying in ionic strength have been used to calculate the dissociation constant of hydrogen fluoride and to validate the response of the latter electrode in strongly acidic media containing fluoride ions.

СПЕКТРОСКОПИЯ В ОТДЕЛЕННЫХ ПЛАМЕНАХ—IV. ИСПОЛЬЗОВАНИЕ ОТДЕЛЕННОЙ АЗОТОМ ПЛАМЕНИ ВОЗДУХА И АЦЕТИЛЕНА В ПЛАМЕННО-ЭМИССИОННОЙ И АТОМНО-ФЛУОРЕСЦЕНТМОЙ СПЕКТРОСКОПИИ:

R. S. Hobbs, G. F. Kirkbright, M. Sargent and T. S. West, *Talanta*, 1968, **15**, 997.

Резюме—Первичные и вторичные комбинационные зоны пламени воздуха и ацетилена разделены струей азота, параллельной пламени, чтобы предотвращать доход атмосферического кислорода к его основе. Пламя является весьма устойчивым в широком диапазоне смесей топлива и воздуха, а органические растворители можно легко взбрызгивать. Низкий фон пламени позволает измерять термическую эмиссию и атомную флуоресценцию с высокой чувствительностью. На пример, висмут определяли в пределах 5–200 мг/л на основе его термической эмиссии при 306,8 ммк, с пределом обнаружения 2 мг/л в водном растворе, а в пределах 1–10 мг/л с пределом обнаружения 0,3 мг/л в 50% тном растворе этилового спирта. Цинк и кадмий определяли при 213,9 и 228,8 ммк методом атомно-флуоресцентной спектроскопии в этой пламени с пределами обнаружения 2×10^{-4} мг/л и 5×10^{-4} мг/л, соответственно, с использованием ламп парового разряда в качестве источников возбуждения. Полученные результаты представляют собой значительное улучшение результатов полученных обыкновенным пламенем воздуха и ацетилена.

ОЦЕНКА ОТВЕТА ЭЛЕКТРОДА С МЕМБРАНОЙ ФТОРИДА ЛАНТАНА В КИСЛЫХ РАСТВОРАХ: ОПРЕДЕЛЕНИЕ pK_a ФТОРИСТОВОДОРОДНОЙ КИСЛОТЫ:

N. E. Vanderborgh, *Talanta*, 1968, **15**, 1009.

Резюме—Результатами измерений, проведенных в сильнокислых растворах с переменной ионной силой, с использованием комбинации стеклянного электрода и электрода с мембраной фторида лантана пользовались для вычисления константы диссоциации фтороводорода и для утверждения ответа последного электрода в содержающих фторидионы сильнокислых средах.

Determination of submicromolar concentrations of fluoride in biological samples: Donald R. Taves, *Talanta*, 1968, **15**, 1015 (Department of Radiation Biology and Biophysics, University of Rochester School of Medicine and Dentistry, Rochester, New York 14620, U.S.A.)

Summary—The fluorescence of a Morin–thorium complex provides a more sensitive fluoride reagent than has been previously used. It has immediate stability and a linear response to fluoride up to 50% reduction in fluorescence. The values for serum fluoride, as measured with this reagent after diffusion at room temperature, agree with those obtained with the fluoride electrode and with those predicted by the renal clearance of radioactive fluoride. The relative standard deviation when measuring $10^{-6}M$ fluoride in 2 ml of serum is ±10%.

Inorganic polarography in organic solvents—IV. Polarography of metal oxinate complexes in various solvents: R. M. Dagnall and S. K. Hasanuddin, *Talanta*, 1968, **15**, 1025 (Chemistry Department, Imperial College, London, S.W.7.)

Summary—The polarography of 24 metal oxinate complexes extracted into chloroform, IBMK, and ethyl acetate has been investigated, a methanolic solution of lithium chloride being used as base electrolyte. Only 15 complexes gave rise to reduction waves, and interference-free determinations have been developed for indium and thallium(III) in chloroform, and for bismuth, molybdenum and uranium in IBMK. The use of ethyl acetate offered no special advantages, and was the least selective of the three solvents used.

Complexes mixtes des nitrilotriacetates metalliques avec l'acide glutamique ou avec l'acide aspartique: J. Israeli and M. Cecchetti, *Talanta*, 1968, **15**, 1031 (Départment de Chimie, Université de Montréal, Montréal, P.Q., Canada.)

Summary—The metallic nitrilotriacetates react with aspartic acid and glutamic acid and form with them mixed complexes. The formation constants of these complexes were determined.

ОПРЕДЕЛЕНИЕ СУБМИКРОМОЛЯРНЫХ КОНЦЕНТРАЦИЙ ФТОРИДА В БИОЛОГИЧЕСКИХ ОБРАЗЦАХ:

DONALD R. TAVES, *Talanta*, 1968, **15**, 1015.

Резюме—Флуоресценция комплекса тория с морином представляет собой более чувствительный реагент для фторида от обыкновенных реагентов. Устойчивость комплекса получается немедленно, а ответ фторида линейный до 50 % тного снижения флуоресценции. Величины для фторида в сыворотке, определенные этим реагентом после диффузии при комнатной температуре соглашаются с результатами, полученными с фторидным электродом и с результатами предсказанными на основе почечной очистки радиоактивного фторида. Относительная стандартная ошибка при определении $10^{-6}M$ фторида в 2 мл сыворотки равна ±10 %.

НЕОРГАНИЧЕСКАЯ ПОЛЯРОГРАФИЯ В ОРГАНИЧЕСКИХ РАСТВОРИТЕЛЯХ—IV. ПОЛЯРОГРАФИЯ ОКСИНАТОВ МЕТАЛЛОВ В РАЗЛИЧНЫХ РАСТВОРИТЕЛЯХ:

R. M. DAGNALL and S. K. HASANUDDIN, *Talanta*, 1968, **15**, 1025.

Резюме—Исследована полярография 24 оксинатов металлов экстрагированных хлороформом, изобутилметилкетоном и этилацетатом, с использованием раствора хлорида лития в метиловом спирте в качестве основного электролита. Восстановительные волны получены только в случае 15 комплексов. Разработаны свободные от влияния процедуры для опуеделения индия и таллия(III) в хлороформе и висмута, молибдена и урана в изобутилметилкетоне. Этилацетат не показал особенных преимуществ и оказался наименее избирательным из трех исследованных растворителей.

СМЕШАННЫЕ КОМПЛЕКСЫ НИТРИЛОТРИАЦЕТАТОВ МЕТАЛЛОВ С ГЛУТАМИНОВОЙ ИЛИ АСПАРАГИНОВОЙ КИСЛОТАМИ:

J. ISRAELI and M. CECCHETTI, *Talanta*, 1968, **15**, 1031.

Резюме—Нитрилотриацетаты металлов реагируют с аспарагиновойиглутам и новой кислотами с образованием смешанных комплексов. Определены константы образования этих комплексов.

Potentiometric studies on the formation of metal complexes with *trans*-1, 2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetra-acetic acid—I. Protonation of the ligand: KNUT SCHRØDER, *Talanta*, 1968, **15**, 1035 (Norges laererhøgskole, Kjemisk institutt, Trondheim, Norway.)

Summary—The protonation of *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetra-acetic acid is studied potentiometrically with the hydrogen electrode. The formation constants have been re-evaluated at 25·0° at an ionic strength of 3·0 ($NaClO_4$), with a least-squares treatment of the data. The potentiometric data are explained from the law of mass action, using a model which assumes five different ligands to be present in the solution; the logarithmic stepwise stability constants are then 9·90, 6·72, 3·65 and 3·21 for the mono-, di-, tri- and tetra-protonated ligand respectively.

Analytical applications of hydroxycoumarins: MOHAN KATYAL and H. B. SINGH, *Talanta*, 1968, **15**, 1043 (St. Stephen's College, Delhi-7, India.)

Summary—A review is presented of the analytical potentialities and physico-chemical properties of hydroxycoumarins.

New chromogens of the ferroin type—III. Some 2-substituted benzimidazole derivatives: ALFRED A. SCHILT and KEITH R. KLUGE, *Talanta*, 1968, **15**, 1055 (Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115, U.S.A.)

Summary—A spectrophotometric study has been made of the iron(II) and copper(I) chelates of 23 new compounds that contain the ferroin functional grouping. Although none of the compounds proved to be superior to chromogenic reagents currently in use, the results are of interest from the point of view of designing new chromogens for iron and copper.

ИЗУЧЕНИЕ ПОТЕНЦИОМЕТРИЧЕСКИМ МЕТОДОМ ОБРАЗОВАНИЯ КОМПЛЕКСОВ МЕТАЛЛОВ С ТРАНС-1,2-ДИАМИНОЦИКЛОГЕКСАН-N,N,N′,N′-ТЕТРАУКСУСНОЙ КИСЛОТОЙ—I. ПРОТОНАЦИЯ ЛИГАНДА:

KNUT SCHRØDER, *Talanta*, 1968, **15**, 1035.

Резюме—Протонация транс-1,2-диаминоциклогексан-N,N,N′, N′-тетрауксусной кислоты изучена потенциометрическим методом, с использованием водородного электрода. Снова определены константы образования при 25,0° и ионной концентрации 3,0 ($NaClO_4$), а результаты обработаны методом наименьших квадратов. Потенциометрические данные объясняются на основе закона действующих масс, пользуясь моделью предполагающей присутствие в растворе пять различных лигандов. Вычисленные логарифмические ступенчатые константы устойчивости равны 9,90, 6,72, 3,65 и 3,21 для моно-, ди-, три- и тетрапротонованного лиганда, соответственно.

ИСПОЛЬЗОВАНИЕ ОКСИКУМАРИНОВ В АНАЛИЗЕ:

MOHAN KATYAL and H. B. SINGH, *Talanta*, 1968, **15**, 1043.

Резюме—Приведен обзор используемости в анализе и физикохимических свойств оксикумаринов.

НОВЫЕ ХРОМОГЕНЫ ТИПА ФЕРРОИНА—III. НЕКОТОРЫЕ 2-ЗАМЕЩЕННЫЕ ПРОИЗВОДНЫЕ БЕНЗИМИДАЗОЛА:

ALFRED A. SCHILT and KEITH R. KLUGE, *Talanta*, 1968, **15**, 1055.

Резюме—Изучены спектрофотометрическим методом хелаты железа(II) и меди(I) с 23 новыми соединениями, содержающими функциональную группу ферроина. Ни одно из исследованных соединений не оказалось лучшим обычно использованных хромогенных реагентов, но результаты интересны для синтезирования новых хромогенов для железа и меди.

Differential spectrophotometry of nickel as its pyridine-2,6-dicarboxylic acid complex: G. den Boef and H. Poppa, *Talanta*, 1968, **15**, 1058 (Laboratory for Analytical Chemistry, University of Amsterdam, Amsterdam, The Netherlands.)

Summary—The determination of nickel with pyridine-2,6-dicarboxylic acid by means of differential spectrophotometry at 1025 mμ is described. At the Ni concentration level of 2 mg/ml the relative standard deviation is 0·1%. Only a few elements interfere.

Homogeneous nucleation of bis(1,2-cyclohexanedionedioximato)-palladium(II): J. A. Velázquez and O. E. Hileman, Jr., *Talanta*, 1968, **15**, 1060 (Department of Chemistry, McMaster University, Hamilton, Ontario, Canada.)

Summary—Precipitation from homogeneous solution has been applied to the drop technique for the study of the homogeneous nucleation of bis(1,2-cyclohexanedionedioximato)palladium(II). It was found that under the experimental conditions employed the interfacial energy of the chelate was 47 ergs.cm^{-2} and the critical radius size 11 Å.

ДИФФЕРЕНЦИАЛЬНАЯ СПЕКТРОФОТОМЕТРИЯ НИКЕЛЯ В ФОРМЕ КОМПЛЕКСА С ПИРИДИН-2,6-ДИКАРБОНОВОЙ КИСЛОТО:

G. DEN BOEF and H. POPPA, *Talanta*, 1968, 15, 1058.

Резюме—Описано определение никеля пиридин-2,6-дикарбоновой кислотой методом дифференциальной спектрофотометрии при 1025 ммк. При концентрации никеля 2 мг/л относительная стандартная ошибка равна 0,1 %. Только немногие элементы мешают определению.

ГОМОГЕННАЯ НУКЛЕАЦИЯ БИС(1,2-ЦИКЛОГЕКСАНДИОНДИОКСИМАТО)-ПАЛЛАДИЯ(II):

J. A. VELÁZQUEZ and O. E. HILEMAN, JR., *Talanta*, 1968, **15**, 1060.

Резюме—Осаждение из гомогенного раствора применено в методе капли для изучения гомогенной нуклеации бис(1,2-циклогександиондиоксимато)палладия(II). В использованных условиях опыта определены межповерхностная энергия хелата 47 эрг.см$^{-2}$, а критический радиус 11 Å.

SUMMARIES FOR CARD INDEXES

Rapid determination of copper in plants by neutron activation analysis: Apostolos P. Grimanis, *Talanta*, 1968, **15**, 279 (Chemistry Department, Nuclear Research Center "Democritos", Aghia Paraskevi, Attikis, Athens, Greece.)

Summary—A rapid and simple neutron-activation analysis method has been developed for the determination of copper in plant leaves Irradiated samples are dissolved in a mixture of fuming nitric acid, 70% perchloric acid and concentrated sulphuric acid in the presence of copper carrier solution. The copper in the resulting solution is extracted as copper cupferronate into chloroform and back-extracted into concentrated ammonia solution. The copper is precipitated as sulphide wih 3% aqueous thioacetamide solution and the precipitate is dissolved in nitric acid. The induced activity of copper-64 in the resulting solution is counted with a 400-channel analyser. The photopeak of the annihilation energy of copper-64 at 0·51 MeV is compared with that of a copper standard processed in the same manner. After counting, the chemical yield of the separated copper is found by re-irradiating aliquots of the copper nitrate solution and comparing the induced activity of copper-66 at 1·04 MeV with that of another standard processed in a similar manner. The time required to complete the analysis, including the second irradiation and all radioactivity measurements, is about 25 min. The accuracy of the method was checked by analysing a biological standard of known copper content. The proposed method was successfully applied to the determination of copper in the leaves of 10 different plants (copper content 4–30 ppm).

Anion-exchange separation of metal ions in dimethyl sulphoxide–methanol–hydrochloric acid: James S. Fritz and Marcia Lehoczky Gillette, *Talanta*, 1968, **15**, 287 (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A)

Summary—The effect of dimethyl sulphoxide on the anion-exchange behaviour of many metals in a methanolic system with hydrochloric acid and explored. Distribution coefficients for 26 elements were determined in a mixed solvent system of dimethyl sulphoxide–methanol–0·6*M* hydrochloric acid, in which the proportions of dimethyl sulphoxide and methanol were varied. Lead(II) and silver(I) complexes are soluble in this system. Interesting effects were noted for gold(III), iron(III), molybdenum(VI) and uranium(VI). As a measure of the usefulness of the systems studied, 27 anion-exchange separations of two- to four-component mixtures of metal ions were carried out, each with quantitative results.

БЫСТРОЕ ОПРЕДЕЛЕНИЕ МЕДИ В РАСТЕНИЯХ МЕТОДОМ НЕЙТРОННОАКТИВАЦИОННОГО АНАЛИЗА:

Apostolos P. Grimanis, *Talanta*, 1968, **15** 279.

Резюме—Разработан быстрый и несложный метод нейтронноактивационного анализа для определения меди в листьях растений. Облученные пробы растворяют в смеси дымящей азотной кислоты, 70 % тной хлорной кислоты и концентрированной серной кислоты в присутствии раствора-носителя меди. Мед из полученного раствора извлекают в форме купферроната меди хлороформом и вторично извлекают концентрированным раствором аммиака. Медь осаждают в форме сульфида 3 % тным водным раствором тиоацетамида, а осадок растворяют в азотной кислоте. Индуцированную активность меди-64 в полученном растворе считают на 400-канальном счетчике. Фотопик энергии уничтожения меди-64 при 0,51 Мэв сравнивают с пиком полученным на обработанном таким же образом эталоне меди. После счета химический выход выделенной меди получают вторичным облучением аликвотных частей раствора нитрата меди и сравниванием индуцированной энергии меди-66 при 1,04 Мэв с активностью другого обработанного таким же образом эталона. Продолжительность комплетного анализа, включая вторичное облучение и все измерения радиоактивности около 25 мин. Точность метода испытана на примере биологического эталона с знакомым содержанием меди. Предложеным методом успешно пользовались для определения меди в листьях 10 различных растений, содержающих 4–30 мкг/г меди.

АНИОНООБМЕННОЕ РАЗДЕЛЕНИЕ ИОНОВ МЕТАЛЛОВ В РАСТВОРАХ ДИМЕТИЛСУЛЬФОКСИДА, МЕТИЛОВОГО СПИРТА И СОЛЯНОЙ КИСЛОТЫ:

James S. Fritz and Marcia Lehoczky Gillette *Talanta*, 1968, **15**, 287.

Резюме—Исследовано влияние диметилсульфоксида на анионообменные характеристики ряда металлов в системе метилового спирта и соляной кислоты. Определены коэффициенты распределения 26 элементов в системе диметилсульфоксидметиловый спирт-0,6*M* соляная кислота, в котором варыровали отношение диметилсульфоксида и метилового спирта. В этой системы растворими комплекси свинца(II) и серебра(I). Интересные эффекты обнаружены в случае золота(III), железа(III), молибдена(VI) и урана(VI). Чтобы показалась полезность изученных систем, провелось 27 анионообменных разделенйи двух- до четырехкомпонентных смесей ионов металлов, с получением количественных результатов.

Die Anwendung von Komplexbildnern in der polarographischen Analyse anorganischer Verbindungen—XIII. Polarographischen Verhalten der Komplexverbindungen des Mangans mit Mannit: Jan Doležal und Oswald Gürtler, *Talanta*, 1968, **15**, 299 (Lehrstuhl für analytische Chemie, Karls-Universität, Prag, Tschechoslowakei.)

Summary—The formation of manganese-mannitol complexes in alkaline solution has been studied polarographically, and it has been shown that manganese(II) hydroxide is oxidized by oxygen or hydrogen peroxide to the brown manganese(III)-mannitol complex and then to the red manganese(IV)-mannitol complex. At the dropping mercury electrode, the manganese(III)-mannitol → manganese(IV)-mannitol system is reversible, with $E_{1/2} = -0{\cdot}375$ V. The probable reaction mechanism is discussed. Manganese may be determined polarographically in the presence of a 20-fold excess of copper in a solution $3M$ in potassium hydroxide and $0{\cdot}5M$ in mannitol, at concentrations down to $10^{-4}M$. When the solution also contains ethylenediamine ($0{\cdot}5M$), interferences from cobalt and iron(III) are removed. The $E_{1/2}$ values for 21 cations in this electrolyte are reported. The method has been applied to the determination of manganese in dolomites and slates.

Extraction of titanium(IV) gallate into tri-iso-octylamine and its spectrophotometric determination: V. T. Athavale, Kulumani R. Krishnamurthy and Ch. Venkateswarlu, *Talanta*, 1968, **15**, 315 (Analytical Division, Bhabha Atomic Research Centre, Trombay, Bombay-74, India.)

Summary—Extraction of titanium(IV) gallate species into tri-iso-octylamine (TIOA) has been studied to develop a spectrophotometric method for the determination of titanium. The behaviour of common ions, under the conditions for quantitative extraction of titanium, is reported. Examples are given of application of the method to analysis of steels, reactor-grade thoria, and silicate rocks.

Calmagite as a spectrophotometric reagent for aluminium: Colin Woodward and Henry Freiser, *Talanta*, 1968, **15**, 321 (Department of Chemistry, University of Arizona, Tucson, Arizona 85721, U.S.A.)

Summary—Calmagite is proposed as a sensitive spectrophotometric reagent for aluminium, $\varepsilon_{570\,\mathrm{m}\mu} = 42000$. After aqueous phase reaction at pH 8·6, the metal–reagent complex is extracted into chloroform by formation of an ion-association complex with a quaternary ammonium salt. The method is free from interference by common anions, and cationic interferences may be eliminated by the use of cyanide and EDTA as masking agents.

ИСПОЛЬЗОВАНИЕ КОМПЛЕКСООБРАЗОВАТЕЛЕЙ В АНАЛИЗЕ НЕОРГАНИЧЕСКИХ СОЕДИНЕНИЙ ПОЛЯРОГРАФИЧЕСКИМ МЕТОДОМ:—XIII. ПОЛЯРОГРАФИЧЕСКАЯ ХАРАКТЕРИСТИКА КОМПЛЕКСНЫХ СОЕДИНЕНИЙ МАРГАНЦА И МАННИТА:

JAN DOLEŽAL und OSWALD GÜRTLER, *Talanta*, 1968, **15**, 299.

Резюме—Образование комплексов марганца-маннитола в щелочном растворе изучено полярографически, и установлено, что кислород или перекись водорода окисляет гидроокись марганца(II) к коричневому комплексу марганца(III)-маннитола и затем к красному комплексу марганца(IV)-маннитола. При капельном ртутном электроде марганец(III)-маннитол → марганец(IV)-маннитол система обратима, при $E_{1/2} = -0,375$ V. Обсуждают возмозный ход реакции. Марганец определяли полярографическим методом в присутствии 20 кратного избытка меди в растворе $3M$ в гидроокиси калия и $0,5M$ в маннитоле, а при концентрациях до $10^{-4}M$. Влияние кобальта и железа(III) удаляется добавлением раствору этилендиамина ($0,5M$). Сообщены величины $E_{1/2}$ для 21 катионов в этом электролите. Методом пользовались для определения марганца в доломитах и сланцах.

ЭКСТРАГИРОВАНИЕ ГАЛЛАТА ТИТАНА(IV) ТРИИЗООКТИЛАМИНОМ И ЕГО ОПРЕДЕЛЕНИЕ СПЕКТРОФОТОМЕТРИЧЕСКИМ МЕТОДОМ:

V. T. ATHAVALE, KULUMANI R. KRISHNAMURTHY and CH. VENKATESWARLU, *Talanta*, 1968, **15**, 315.

Резюме—Изучена экстракция галлата титана(IV) триизооктиламином (ТИОА) с целью разработать спектрофотометрический метод определения титана. Сообщена характеристика обыкновенных ионов в условиях количественного извлечения титана. Даны примеры использования метода для анализа сталей, окиси тория реакторной чистоты и силикатных горных пород.

КАЛМАГИТ В КАЧЕСТВЕ СПЕКТРОФОТОМЕТРИЧЕСКОГО РЕАГЕНТА ДЛЯ АЛЮМИНИЯ:

COLIN WOODWARD and HENRY FREISER, *Talanta*, 1968, **15**, 321.

Резюме—Калмагит предложен в качестве чувствительного спектрофотометрического реагента для алюминия, $\varepsilon_{570 mm\mu} = 42000$. После реакции в водной фазе при pH 8,6 комплекс металл-реагент экстрагируют хлороформом, образованием ионоассоциационного комплекса с солью четвертичного аммониевого основания. Обыкновенные анионы не мешают определению, а влияние катионов исключается использованием цианидиона и ЭДТА в качества маскирующих агентов.

Determination of nitrogen in an aluminium-killed steel by an isotope-dilution method using $Al^{15}N$: Keiichi Furuya, Shoichiro Okuyama, Takashi Tachikawa and Hitoshi Kamada: *Talanta*, 1968, **15**, 327 (Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo, Japan.)

Summary—Nitrogen in an aluminium-killed steel was determined by an isotope-dilution method using synthesized aluminium nitride enriched with ^{15}N. The results were in agreement with those obtained by chemical determination, whereas the vacuum fusion method with iron and platinum baths, and the isotope-dilution method using gaseous ^{15}N-enriched nitrogen, did not give accurate results.

Rapid visual compleximetric titration of calcium in natural waters: B. Fleet, Soe-Win and T. S. West, *Talanta*, 1968, **15**, 333 (Chemistry Department, Imperial College, London, S.W.7, U.K.)

Summary—Visual compleximetric methods for the titration of calcium in the presence of magnesium have been based either on masking the magnesium or using an indirect indicator procedure, *e.g.*, the system Zn–EGTA–Zincon. In the proposed method these two approaches are combined. Zn–EGTA complex is added to the mixture and the zinc liberated in the calcium replacement reaction is titrated with EGTA after the magnesium has been masked with fluoride ion.

Anion-exchange behaviour of the platinum metals and gold in hydrochloric acid–organic solvent media: J. Korkisch and H. Klakl, *Talanta*, 1968, **15**, 339 (Analytical Institute, University of Vienna IX, Währingerstrasse 38, Austria.)

Summary—The anion-exchange characteristics of the platinum metals and gold in hydrochloric acid media are described. The distribution coefficients of these elements were measured on the strongly basic anion-exchange resin Dowex 1 × 8 in mixtures of hydrochloric acid with water and several organic solvents, *i.e.*, dimethylformamide, acetone, tetrahydrofuran, dioxan, methanol, acetic acid and pyridine. Based on these data the conditions most suitable for quantitative separation are indicated and discussed.

ОПРЕДЕЛЕНИЕ АЗОТА В УСПОКОЕННОЙ АЛЮМИНИЕМ СТАЛИ МЕТОДОМ РАЗБАВЛЕНИЯ ИЗОТОПОВ, ПОЛЬЗУЮЩИМСЯ С Al^{15}N:

Keiichi Furuya, Shoichiro Okuyama, Takashi Tachikawa and Hitoshi Kamada: *Talanta*, 1968, **15**, 327.

Резюме—Азот в успокоенной алюминием стали определяли методом разбавления изотопов, пользуясь синтезированным нитридом алюминия, обогащенным с ^{15}N. Полученные результаты соглашались с результатами полученными химическим методом, но метод плавления в вакууме с железной и платиновой банями и метод разбавления изотопов, пользующийся газообразным обогащенным с ^{15}N азотом не дали точные результаты.

БЫСТРОЕ ВИЗУАЛЬНОЕ КОМПЛЕКСОНОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ КАЛЬЦИЯ В ПРИРОДНЫХ ВОДАХ:

B. Fleet, Soe-Win and T. S. West, *Talanta*, 1968, **15**, 333.

Резюме—Визуальные комплексонометрические методы титрования кальция в присутствии магния основываются либо на маскировании магния либо на процедуры пользующейся непрямым индикатором, на пример системы Zn–ЭГТА–цинкон. Предложенный метод комбинирует эти два принципа. Смеси добавляют Zn–ЭГТА комплекс, а цинк, выделенный в реакции обмена кальция, титруют с ЭГТА после маскирования магния фторидионом.

АНИОНООБМЕННЫЕ ХАРАКТЕРИСТИКИ ПЛАТИНОВЫХ МЕТАЛЛОВ И ЗОЛОТА В РАСТВОРАХ СОЛЯНОЙ КИСЛОТЫ И ОРГАНИЧЕСКИХ РАСТВОРИТЕЛЕЙ:

J. Korkisch and H. Klakl, *Talanta*, 1968, **15**, 339.

Резюме—Описаны анионообменные характеристики платиновых металлов и золота в солянокислых средах. Определены коэффициенты распределения этих элементов на сыльноосновной анионообменной смоле Дауекс 1 × 8, в смесях соляной кислоты, воды и ряда органических растворителей: диметилформамида, ацетона, тетрагидрофурана, диоксана, метилового спирта, уксусной кислоты и пиридина. На основании этих данных отбраны и обсуждены самые подходящие условия для количественного разделения.

Argentometric coulometric titration of thioacetamide: D. M. King and W. S. Eaton, *Talanta*, 1968, **15**, 347 (Department of Chemistry, Western Washington State College, Bellingham, Washington, U.S.A.)

Summary—The coulometric determination of thioacetamide (TAA) with electrogenerated silver is described. The titration is done in a solution 0·1*M* in both ammonia and sodium hydroxide, and the end-point is detected potentiometrically with a silver–silver sulphide electrode. On repeat analyses of approx. 2-mg samples of TAA an average error of −0·4% (relative standard deviation 0·25%) was obtained. Important steps in the procedure include cleaning the silver generating electrode in nitric acid before each titration, purging well with nitrogen to remove oxygen, and not using too large a sample.

Oxidation of some sugars with copper(III): S. Chandra and K. L. Yadava, *Talanta*, 1968, **15**, 349 (Chemical Laboratories, University of Allahabad, Allahabad, India.)

Summary—The titrimetric determination of glucose, fructose, mannose, galactose, arabinose, xylose and sucrose with potassium ditelluratocuprate(III) is described. On heating, pentoses and hexoses consume 20 and 24 equivalents of copper(III) per mole respectively, and sucrose consumes 48 equivalents.

Spectrophotometric titration of bismuth with EDTA: N. A. Ramaiah, G. D. Tewari, S. R. Trivedi and Sarvagya S. Katiyar, *Talanta*, 1968, **15**, 352 (Department of Chemistry, Indian Institute of Technology, Kanpur, India.)

Summary—A new spectrophotometric method for the estimation of bismuth with EDTA, using iron–salicylate complex as the indicator, has been developed. The determinations were carried out by measuring the absorbance at 520 mμ of solutions containing bismuth, iron(III), salicylic acid and various quantities of EDTA, at pH 0·5. It has been shown from the stability constants of the complexes present that before the end-point iron(III) will not react appreciably with the Bi–EDTA complex. The interference from iron(III) in the estimation of bismuth, which is a serious drawback in many other methods, is eliminated in the present method, as iron(III) acts as the indicator.

АРГЕНТОМЕТРИЧЕСКОЕ КУЛОНОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ ТИОАЦЕТАМИДА:

D. M. KING and W. S. EATON, *Talanta*, 1968, **15**, 347.

Резюме—Описано кулонометрическое определение тиоацетамида (ТАА) с электролитически генерированным серебром. Титрация выполнена в растворе содержащем 0,1M аммиака и гидроокиси натрия, а конец титрования обнаружен потенциометрическим методом, с использованием электрода серебросульфид серебра. В повторных анализах проб от приблизительно 2 мг ТАА получена средная ошибка −0,4% (относительная стандартная ошибка 0,25%). Важными операциями для успешного титрования являются очистка серебряного генерирующего электрода в азотной кислоте пред каждым титрованием и продувка раствора азотом для удаления кислорода; кроме того не надо отбирать болшие пробы.

ОКИСЛЕНИЕ НЕКОТОРЫХ САХАРОВ МЕДЬЮ(III):

S. CHANDRA and K. L. YADAVA, *Talanta*, 1968, **15**, 349.

Резюме—Описано титриметрическое определение глюкозы, фруктозы, маннозы, галактозы, арабинозы, ксилозы и сахарозы дителлуратокупратом(III) калия. При нагревании пентозы и гексозы потребляют 20 и 24 эквивлентов меди(III) на моль, соответсвенно, а сахароза потребляет 48 эквивалентов

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ ВИСМУТА С ЭДТА:

N. A. RAMAIAH, G. D. TEWARI, S. R. TRIVEDI and SARVAGYA S. KATIYAR, *Talanta*, 1968, **15**, 352.

Резюме—Разработан новый спектрофотометрический метод определения висмута с ЭДТА, пользующийся комплексом железа и салициловой кислоты в качестве индикатора. Определения проводили измерением светопоглощения при 520 ммк растворов содержающих висмут, железо(III), салициловую кислоту и различные количества ЭДТА, при Ph 0,5. Константы устойчивости присутствующих комплексов показали что перед получением конца титрования железо(III) реагирует только в незначительной мере с комплексом Bi-ЭДТА. Влияние железа(III) на определение висмута, представляющее собой серьезный недостаток ряда других методов, избегнуто в этом методем потому что железо(III) служит в качестве индикатора.

results of the newer spectroscopic techniques is a particularly praiseworthy feature. For the teacher there is a companion volume "Supplement for Modern Organic Chemistry" (pp. 525; 325) which contains the answers to the problems, with further discussion where necessary.

Hormone Chemistry: W. R. Butt. Van Nostrand, London, 1967. Pp. xvi + 397. 75s.

Purification of Acetonitrile and Tests for Impurities: J. F. Coetzee. Butterworths, London, 1967. Pp. 7. 3s. (Reprint of *Pure and Applied Chemistry*, 1966, **13** (3), 429–435.)

Preparation of Anhydrous Ethylenediamine: L. M. Mukherjee and S. Bruckenstein. Butterworths, London, 1967. Pp. 6. 3s. (Reprint of *Pure and Applied Chemistry*, 1966, **13** (3), 421–426.)

NOTICES

U.S.A.

30 *June*–5 *July* 1968, **The First International CODATA Conference** on the critical evaluation of numerical property values in the physical sciences will be held at Arnoldshain in the Taunus Mountains near Frankfurt/Main from 30 June to 5 July 1968. This Conference will be under the auspices of the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions (ICSU). It will be run along the informal lines of the Gordon Conferences in the U.S.A. and the EUCHEM Conferences in Europe. The General Chairman of the Conference will be Prof. Dr. W. Klemm, Vice President of CODATA and recently president of IUPAC.

CODATA is a committee of ICSU started in 1966 to stimulate and coordinate informally on a world-wide basis the rapidly growing effort to collect, evaluate, compile and publish the evaluated numerical data of science and technology. Six major countries (France, Germany, Japan, U.K., U.S.A. and U.S.S.R.) and eleven International Unions of ICSU are represented on the committee.

Information and application forms to attend the meeting may be obtained from Dr. Guy Waddington, Executive Director, Central Office, CODATA, c/o National Academy of Sciences, 2101 Constitution Ave. N.W., Washington, D.C. 20418, U.S.A.

DEUTSCHE DEMOKRATISCHE REPUBLIK

18–20 *September* 1968, **Optische Spektralanalyse.** Das Institut für analytische Chemie der Technischen Hochschule für Chemie "Carl Schorlemmer" Leuna-Merseburg veranstalst vom 18–20 September 1968 eine Tagung zum Thema

"Optische Spektranalyse"

In Plenar- und Diskussionsvorträgen soll insbesondere die Bedeutung der Intensität als Stoffkonstante und als analytische Meßgröße in den verschiedenen Bereichen des optischen Spektrums behandelt werden. Dabei stehen im Vordergrund methodische Fortschritte und neuere theoretische Erkenntnisse der Atomspektroskopie (neue Anregungsquellen, Atomabsorption), der Molekülspektroskopie (IR- und UV-Spektroskopie) und auch allgemein interessierende, mit der Intensitätsmessung zusammenhängende metrologische Probleme.

Anmeldungen für Diskussionsvorträge (Zeit 20 min) werden mit kurzer Inhaltsangabe in doppelter Ausfertigung bis 1.3.1968 erbeten an

Institut für analytische Chemie
der Technischen Hochschule für Chemie
"Carl Schorlemmer" Leuna-Merseburg
42 *Merseburg* (DDR)
Geusaer Straße

Anmeldungen für die Teilnahme an dieser Tagung müssen bis 1.4.1968 vorliegen. Alle weiteren Einzelheiten (wissenschaftliches Programm, Damenprogramm, organisatorische. Bisher eingegangene Interessentenmeldungen gelten als Anmeldung und werden berücksichtigt.

Talanta, 1968, Vol. 15, p. ix. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Homogeneous nucleation of bis(1,2-cyclohexanedionedioximato)palladium(II): J. A. Velazquez and O. E. Hileman, Jr. (15 *January* 1968)

Molybdän(VI)–Hydroxylamin–Komplexe—III. Die chelometrische Bestimmung von Molybdän als ternärer Molybdän(VI)–Hydroxylamin–ÄDTA—Komplexe und Vergleich des Verfahrens mit der bereits bekannten Titriermethode von Molybdän(V) mit ÄDTA: Erik Lassner and Hartmann Schedle. (22 *January* 1968)

Determination of scandium in sea-water by atomic-absorption spectroscopy: Yiu-Kee Chau and Pui-Yuen Wong. (23 *January* 1968)

Extraction with tributyl phosphate and direct spectrophotometric determination of molybdenum in the organic phase: Mario Caiozzi M. and Hugo Zunino V. (24 *January* 1968)

Applications of enzyme-catalyzed reactions in trace analysis—III. Determination of silver and thiourea by their combined inhibition of invertase: D. Mealor and A. Townshend. (25 *January* 1968)

Coulometric titration of acids in non-aqueous solvents: J. S. Fritz and F. E. Gainer. (25 *January* 1968)

Estimation of neodymium with aluminun by high frequency technique: G. V. Shivahare and N. D. Joshi. (26 *January* 1968)

Determination of aluminium by plutonium metal by differential linear-sweep oscillographic polarography: C. E. Plock and J. Vasquez. (29 *January* 1968)

On the possibility of using an electromagnetic radioisotope separator in conjunction with charged particle and photon-activation analysis: E. A. Schweikert. (30 *January* 1968)

Spiking of low-grade ore samples in non-destructive activation analysis for gold and uranium: P. W. De Lange, W. J. De Wet and J. H. Venter. (30 *January* 1968)

Polarographic investigation of *syn*-phenyl-2-pyridyl ketoxime: L. W. Harrison and G. E. Cheney. (30 *January* 1968)

Synergic effect in ion-exchange in mixed-solvent media: J. Subrahmanyam and M. N. Sastri. (1 *February* 1968)

Distillation and diffusion methods for the separation of fluorine: Jan Tušl. (5 *February* 1968)

Extension of sensitivity of the determination of molybdenum and tungsten in niobium and tantalum: S. Kallman, E. W. Hobart and H. K. Oberthin. (6 *February* 1968)

Extraction method for determination of zinc(II) with dithizone in the presence of lead(II) and cadmium(II) with dithiocarbaminoacetic acid as masking agent: O. Budevsky, E. Russeva and R. Stoytcheva. (6 *February* 1968)

Interference of the ammonium ion in Mohr's method for the determination of chloride: Erkki Wänninen. (6 *February* 1968)

Photometric determination of palladium with dimethylsulphonazo III: B. Buděšinský and B. Menclová. (7 *February* 1968)

Properties of zirconium compounds likely to be of interest to the analytical chemist: Warren B. Blumenthal. (8 *February* 1968)

Determination of silver by polarography in a solvent composed of dimethylsulphoxide, water, and hydrochloric acid: I. Birze, L. W. Marple and H. Diehl. (8 *February* 1968)

Cation-exchange separation of metals in dimethylsulphoxide–aqueous hydrochloric acid media: I. Birze, L. W. Marple and H. Diehl. (8 *February* 1968)

Inorganic analysis in organic solvents—III. Quantitative relationships in the solvent extraction of chelates: F. R. Haba and D. A. Pantony. (9 *February* 1968)

Eine neue Mikromethode der photokolorimetrischen Bestimmung des Bi(III) mittels des n-phenylamino-thioformyl-N′-phenylamino-thioformylhydrazins: L. Roman, Eugenia Florean and P. Marcu. (9 *February* 1968)

Mass spectra of some bivalent transition–metal ion chelates with pyridylazo-phenols and naphthols: D. Betteridge and D. John. (9 *February* 1968)

Liquid-liquid extraction of selenium(IV) as its bromide into benzene: K. Tanaka. (12 *February* 1968)

Determination of vanadium in ore samples by atomic-absorption spectrophotometry: Rafael Goecke. (12 *February* 1968)

Solubility product of cadmium sulphide: R. Belcher, J. P. C. Farr and A. Townshend. (13 *February* 1968)

Spectrophotometric determination of iodide ions by solvent extraction with Crystal Violet: Y. Yamamoto S. Uchikawa, E. Sumimura and K. Akabori. (13 *February* 1968)

Mixing efficiency and instrumental delay effect on recorded kinetic *f*(*c*) *vs*. *t* curves: Maurizio Caselli Alberto Cavaggioni and Paolo Papoff. (14 *February* 1968)

Voltammetric study of molybdenum reduction: V. P. Apte and R. G. Dhaneshwar. (14 *February* 1968)

Talanta, 1968, Vol. 15, p. v. Pergamon Press. Printed in Northern Ireland

NOTICE

CZECHOSLOVAKIA
FIFTH RADIOCHEMICAL CONFERENCE: 19–24 May 1969

The Czechoslovak Chemical Society of the Czechoslovak Academy of Science, Nuclear Chemistry Section, Zvíkov, will organize this conference, the topic being separation methods, especially solvent extraction and ion-exchange. The working language is English; any language can be used for presentation of a paper, but the full text in English must be made available. Further information may be obtained from Ing. J. Alexa, C.Sc., Institute for Nuclear Research, Řež near Prague, Czechoslovakia.

ADVISORY BOARD OF TALANTA

K ISSLEIB (German Democratic Republic) studied chemistry at Friedrich Schiller University from 1939 (studies interrupted by World War II) until 1950 when he obtained his Doctorate degree. His scientific career began in 1949 as an Assistant at the Institute for Inorganic Chemistry at Jena under the direction of Fr Heim; in 1952 he was nominated Head Assistant and Lecturer in analytical chemistry—particularly chromatography and gas analysis—and eventually became Dozent. In 1960 he moved to Martin Luther University Halle-Wittenberg, where he was appointed Director of the Institute for Inorganic Chemistry in 1963. Professor Issleib's interests are in the field of complex chemistry, especially of phosphorus and antimony, including structural problems After formation of the Analytical Chemistry Section of the Chemical Society of the German Democratic Republic, he was its Chairman until 1964.

ADVISORY BOARD OF TALANTA

The Editorial Board and Publishers of *Talanta* take pleasure in welcoming the following new members to the Advisory Board of the journal

E. CERRAI K. ISSLEIB
M. DIMBAT R. E. SIEVERS
R. E. WAINERDI

Also, they would like to record their sincere thanks for the help given by

F. E. CRITCHFIELD W. RIEMAN III
J. O. HIBBITS E. L. SIMONS

who retire from the Advisory Board.

Born in 1924, ENRICO CERRAI (Italy) received his doctorate at Pisa University in 1949. Subsequently, he started research into deuterium separation and measurement at C.I.S.E. (Milano), where in 1956 he was charged with the organization of the Chemistry and Radiochemistry Laboratories. Since 1950 he has also belonged to the teaching staff of Politecnico, Milan, which activities earned him the title of Professor of Nuclear Chemistry in 1960. He has developed new analytical and separative methods of various elements, and techniques based on liquid-liquid extraction and reversed-phase chromatography. In 1967 he was appointed General Director of C.I.S.E.

MARTIN DIMBAT (U.S.A.) was born in 1920 in Oelwei a small town in Iowa. He holds an M.S. degree from th State University of Iowa in 1948. Since that time he ha been active in analytical research with Shell Developme Company in Emeryville, California. His early wor culminated in a book entitled "Number Average Molecula Weights" coauthored with F. H. Stross and R. U. Bonna Some of the very early development work on gas chromato raphy was done in the Shell laboratories by Mr. Dimb and coworkers. The past several years have been spent i research on the fractionation of polymers and their identif cation by pyrolysis-gas chromatography.

ROBERT E. SIEVERS (U.S.A.) was born in 1935, receiv
his B.S. (1956) from University of Tulsa, and his M.
(1958) and Ph.D. (1960) from University of Illinois, whe
he studied metal complexes of polyaminocarboxylic aci
under the direction of Professor John C Bailar, Jr. He
presently Director of the Inorganic and Analytic
Chemistry Group of the Aerospace Research Laboratori
Wright-Patterson Air Force Base, Ohio. For seve
years he has conducted research on the gas chromatograp
of metal chelates. His research interests include ultra-tra
metal analysis by gas chromatography, stereochemistry a
nuclear magnetic resonance spectroscopy of metal c
ordination compounds, and the resolution and isomerizati
of metal chelates. Dr. Sievers presently serves as Pr
gramme Chairman for the Inorganic Division of t
American Chemical Society.

RICHARD E. WAINERDI (U.S.A.) is professor of Chemical Engineering and Associate Dean of Engineering at Texas A & M University. He received his B.S. from University of Oklahoma (1952) and the M.S. (1955) and Ph.D. (1958) degrees from Pennsylvania State University. After attending the Oak Ridge School of Reactor Technology 1955–56, Professor Wainerdi came to Texas A & M to develop a nuclear programme for the University. He established the Activation Analysis Research Laboratory in 1957, and has been working in the areas of automated computer coupled activation analysis including miniaturized systems since that time. His special interests are in applications of nuclear activation analysis to problems of biochemistry, geochemistry and metallurgy, as well as basic methodology research.

AUTHOR INDEX

PRINTED IN NORTHERN IRELAND AT THE UNIVERSITIES PRESS, BELFAST

Talanta, 1968, Vol. 15, p. vii. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Coulometry in Analytical Chemistry: G. W. C. MILNER. Pergamon, Oxford, 1968. Pp. 207. Hard cover 30s. Flexi-cover 21s.

This is an excellent introduction to the subject, which should be of value to senior undergraduates and to all chemists who feel that coulometry might be of use to them. A good choice of reprinted articles describing the development of this branch of analytical chemistry forms the second half of the book. A comprehensive literature survey is presented in tabular form. There are chapters on Theory, Constant-current coulometry, Controlled-potential coulometry, Applications, and Coulometric titrations.

Introduction aux méthodes électrochimiques: Ed. J. ROBIN. Masson, Paris, 1967. Pp. 357, Fig. 225. Soft cover 65 NF.

This volume is a collection of articles originally written as part of a refresher-course on electro-analytical chemistry given in Lyon in 1964 and 1965, and now revised for publication in this text. The book consists of two parts, on voltammetry and polarography, and chapters cover these fields comprehensively, dealing with theory, instrumentation and techniques, and applications. The text is well illustrated, and can be recommended for senior undergraduates and all chemists interested in electro-analytical techniques.

La catalyse au laboratoire et dans l'industrie: Ed. B. CLAUDEL. Masson, Paris, 1967. Pp. 330, Fig. 110. Soft cover 60 NF.

This text contains the basis of the course on catalysis offered at the National Institute for Applied Sciences at Lyon. There are main sections on Mechanisms of catalytic reactions, The study of heterogeneous catalysis, and Practical examples of catalysis in industrial processes. A useful advanced text.

Lipid Chromatography Analysis Vol. 1. GUIDO V. MARINETTI. Edward Arnold, London, 1967. Pp. xv + 537. £10. 10.

This book, the first of a two-volume set, presents a very full coverage of chromatographic methods in a field where no comparably comprehensive text is available. It deals with the fractionation of phosphatides, glycolipids, neutral glycerides, fatty acids, alkoxy lipids and of long-chain aldehydes by paper, thin-layer, column and gas-liquid chromatography and there are chapters on the fractionation of sphingosine and related compounds, on inositol and glycerol, on the carbohydrates in glycolipids and on nitrogen bases derived from lipids. The book is well written, detailed and should prove of considerable value as a source of knowledge not only on major, but on the often more valuable minor, points of technique. It is well produced but rather expensive.

Steroid Hormone Analysis, Vol. 1: Ed. HANS CARSTENSEN. Edward Arnold, London, 1967. Pp. xiii + 493. £10. 10.

This is the first of two volumes and serves as an introduction to some current methods of steroid hormone determination. The content is rather more specialized than the title suggests, but should be valuable to research workers in clinical chemistry, although of only limited interest to the pharmaceutical analyst. There are chapters on Isotope derivative methods, Infrared spectroscopy, NMR, Paper and gas chromatography, Testosterone and steroid conjugates, each chapter having a comprehensive reference list. Every attention has been paid to practical detail throughout the book.

Statistik in der analytischen Chemie: K. DOERFFEL. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1966. Pp. 211.

An account of the statistical methods used in analytical chemistry, with examples drawn from classical and instrumental methods. Quality control, regression analysis, the usual statistical parameters, and calculation methods are all dealt with, and there is a useful German-English-Russian statistical vocabulary and a set of tables.

Colorimetric Chemical Analytical Methods, 3 Vols., 7th Ed. Tintometer Ltd., Salisbury, England, 1967. Pp. 493. £7. 7.

A collection of colorimetric methods of analysis for use with the Lovibond Tintometer, these volumes would have been more useful to the practising analyst had wavelengths of maximum absorption been given where appropriate. The purchaser is supplied free with any additional material issued during the two years after publication.

Talanta, 1968, Vol. 15, pp. viii to ix. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Spectrophotometric determination of platinum in experimental catalysts: T. D. REES and S. R. HILL. (28 *November* 1967)

Determination of hydrogen peroxide by xenon trioxide oxidation: R. H. KRUEGER, J. P. WARRINER and BRUNO JASELSKIS. (15 *December* 1967)

Über Eisen(III)-Komplexe mit Phenolen—I. Reaktion zwischen Eisen(III)-Ionen und Monophenolderivaten: G. ACKERMANN and D. HESSE. (26 *December* 1967)

New chromogens of the ferroin type—II. Pyrido and pyridyl derivatives of phenazine and quinoxaline: ALFRED A. SCHILT and WILLIAM C. HOYLE. (25 *January* 1968)

Solvent extraction behaviour of thiocyanic acid: A. JURRAANSE and D. M. KEMP. (30 *January* 1968)

Stability constants of manganese(II) bromide complexes: J. R. FRYER and D. F. C. MORRIS. (1 *February* 1968)

Application of solvent extraction to the refining of precious metals—III. Purification of gold: D. F. C. MORRIS and M. ALI KHAN. (1 *February* 1968)

The importance of Smales's work for improving the quality of the data of geochemistry: L. H. AHRENS. (6 *February* 1968)

Uranium content of sea-water: R. SPENCE. (7 *February* 1968)

Kinetics and mechanisms of the reduction of mercuric chloride by malic acid, induced by potassium peroxydisulphate: KRISHNA KUMAR and L. K. SAXENA. (16 *February* 1968)

Analytical applications of ternary complexes—VI. Elucidation of mode of formation of sensitized metal–chelate systems and determination of molybdenum and antimony: B. W. BAILEY, J. E. CHESTER, R. M. DAGNALL and T. S. WEST. (20 *February* 1968)

Fall-out monitoring of waters—I. Radiochemical determination of caesium-137 and strontium-89, 90 by ion-exchange: M. SENEGAČNIK and Š. PALJK. (21 *February* 1968)

Phase titrations—A new procedure utilizing a clarification end-point: D. A. DUNNERY and G. R. ATWOOD. (22 *February* 1968)

Extraction of gallium with tetraphenylarsonium chloride: H. L. FINSTON and M. S. RAHAMAN. (24 *February* 1968)

Separate determination of sulphates and sulphonates in anionic surfactants: G. W. STRÖHL and D. KURZAK. (27 *February* 1968)

Stability constants of some metal complexes of triethylenetetraminehexaacteic acid and complexometric titration of rare earths and other metals: DONALD A. SOUCEK, K. L. CHENG and HENRY A. DROLL. (27 *February* 1968)

Redox–complexometric determination of iron and cobalt and its application to the analysis of multicomponent alloys: JAN HORÁČEK and RUDOLF PŘIBIL. (28 *February* 1968)

New use of tetrasubstituted ammonium salts in analytical chemistry: M. PANTŮČEK. (28 *February* 1968)

Polarographic study of the substitution reactions of the chelates of triethylenetetraminehexa-acetic acid—I. Reaction of the zinc chelate with calcium ions: MILOSLAV KOPANICA. (28 *February* 1968)

Analytical applications of ternary complexes—VII. Spectrophotometric determination of trace amounts of palladium(II): R. M. DAGNALL, M. T. EL-GHAMRY and T. S. WEST. (29 *February* 1968)

The polarography of arsenic: J. P. ARNOLD and R. M. JOHNSON. (29 *February* 1968)

Stilazokhimdu as photometric reagent for scandium: A. I. Busev, N. N. Basargin and G. E. Lunina. (29 *February* 1968)

Determination of potassium with alkali metal–heavy metal cobaltinitrites: A. H. I. Ben-Bassat. (1 *March*, 1968)

Semi-quantitative determination of nickel, iron and lead on millipore filters: Robert E. Bossart, Frederic J. Feldman and Gary D. Christian. (4 *March* 1968)

New spectroscopic method for studying equilibrium constants and reaction kinetics: R. S. Roy. (4 *March* 1968)

Rapid radiochemical separation of selenium: T. McGee, J. Lynch and G. G. J. Boswell. (4 *March* 1968)

New chromogens of the ferroin-type—III. Some 2-substituted benzimidazole derivatives: Alfred A. Schilt and Keith R. Kluge. (4 *March* 1968)

Elemental analysis of organo-metallic compounds. Automatic combustion in microdetermination of carbon and hydrogen: N. E. Gel'man. (5 *March* 1968)

Structure of metal chelates of arsenazo III, phosphonazo III and sulphonazo III: B. Buděšínský. (7 *March* 1968)

Evaluation of the lanthanum fluoride membrane electrode response in acidic solutions: N. E. Vanderborgh. (7 *March* 1968)

Metal complexes of PAR, TAR and PAN: Alfio Corsini. (8 *March* 1968)

2,5-Dihydroxyacetophenone oxime as an analytical reagent for the colorimetric estimation of molybdenum: B. D. Gupta and Wahid U. Malik. (8 *March* 1968)

Spectrophotometric determination of thallium with 4-(2-pyridylazo)-resorcinol and 4-(2-thiazolylazo) resorcinol: M. Hniličková and L. Sommer. (8 *March* 1968)

Absorptiometric study of Azo Rhodine 2G as a reagent for palladium(II): J. N. Mathur and S. N. Banerji. (11 *March* 1968)

Photometric titrations—XII. A full-immersion spectrophotometer: H. Flaschka and R. Speights. (13 *March* 1968)

Application of alkylphosphoric acids in analytical chemistry. The extraction of gallium from oxy-acid media by mixed solvents: I. S. Levin and N. A. Balakireva. (14 *March* 1968)

Vanadox—a new reagent for photometric determination of vanadium in complex materials: N. S. Frumina, I. S. Mustafin, M. L. Nikurashina and M. K. Vechera. (14 *March* 1968)

Talanta, 1968, Vol. 15, p. x. Pergamon Press. Printed in Northern Ireland

NOTICES

LOUIS GORDON MEMORIAL AWARD

The Editorial Board wish to announce that the Louis Gordon Memorial Award for 1967 is made to Professor H. J. V. TYRRELL for his paper "End-point Sharpness in Thermometric Titrimetry" in *Talanta*, 1967, **14**, 843, which was adjudged the best-written, stylistically, of the year.

PRESS RELEASE

2nd Symposium on Fluorine Chemistry, 1968. The Academy of Sciences at Göttingen in cooperation with the Institute of Inorganic Chemistry of the University at Göttingen prepares the 2nd European Symposium on Fluorine Chemistry from 28–31 August, 1968. The Gesellschaft Deutscher Chemiker has taken over the organisation of the Symposium.

Only discussion lectures and no plenary lectures will be presented at the Symposium.

Chairman of the scientific committee is Prof. Dr. O. Glemser, the president of the Academy of Sciences at Göttingen. Further material for participation in the Symposium and for submitting discussion papers (only until 15 May, 1968) may be asked for at Dr. W. Fritsche, Gesellschaft Deutscher Chemiker, 6000 Frankfurt (M), Postfach 9075, Germany.

PRESSENOTIZ

2. Europäisches Fluorsymposium, 1968. Die Akademie der Wissenschaften zu Göttingen veranstaltet in der Zeit vom 28–31 August 1968 gemeinsam mit dem Anorganisch-Chemischen Institut der Universität Göttingen das 2. Europäische Fluorsymposium. Die organisatorische Vorbereitung des Symposiums hat die Gesellschaft Deutscher Chemiker übernommen.

Auf dem Symposium sollen keine Plenarvorträge, sondern ausschließlich Diskussionsvorträge gehalten werden.

Den Vorsitz des wissenschaftlichen Komitees hat der Präsident der Akademie der Wissenschaften zu Göttingen, Herr Prof. Dr. O. Glemser, übernommen. Unterlagen für die Teilnahme und zu Diskussionsvorträgen, die bis zum 15. Mai 1968 eingereicht werden müssen, können bei Herrn Dr. W. Fritsche, Gesellschaft Deutscher Chemiker, 6000 Frankfurt (M), Postfach 9075, angefordert werden.

Talanta, 1968, Vol. 15, p. x. Pergamon Press. Printed in Northern Ireland

NOTICES

MICROCHEMICAL WORKSHOP—1968

The American Microchemical Society will conduct a Microchemical Workshop, August 22–24 at The Pennsylvania State University.

The programme will consist of morning lectures on a number of topics that are of current interest to the chemist, followed by afternoon sessions devoted to demonstrations of equipment and techniques, laboratory work sessions including instruction in the use of thermal microscopy, and discussion groups. The afternoon laboratory sessions will be in charge of the lecturers who presented the theoretical aspects in the morning sessions.

Topics will include "The Theory and Application of Ion-Specific Electrodes", "Determination of Purity by Thermal Methods", "Thermal Microscopy in the Pharmaceutical Industry", and "Current Status and New Ideas in Fluorine Determination". One day will also be devoted to the general topic of "Current Ideas and Practice in the Operation of Microchemical Laboratories".

It is expected that the following lecturers will participate:

PROFESSOR R. BELCHER, University of Birmingham, England.
DR. N. BRENNER, Perkin-Elmer Corporation, U.S.A.
DR. B. BUDĚŠINSKÝ, Czechoslovak Academy of Sciences, Prague, Czechoslovakia.
DR. A. DIRSCHERL, Hoffmann-LaRoche, A. G., Basel, Switzerland.
DR. ALLAN GRAY, Perkin-Elmer Corporation, U.S.A.
MR. D. KETCHUM, Eastman Kodak Company, U.S.A.
PROFESSOR DR. M. KUHNERT-BRANDSTÄTTER, University of Innsbruck, Austria.
DR. W. PADOWETZ, CIBA, Basel, Switzerland.
DR. JAMES ROSS, Orion Corporation, U.S.A.
DR. W. SCHÖNIGER, Sandoz, A. G., Basel, Switzerland.
PROFESSOR DR. W. SIMON, Eidg. Technische Hochschule, Zürich, Switzerland.
DR. H. WAGNER, J. R. Geigy, S. A., Basel, Switzerland.
PROFESSOR C. WILSON, Queen's University, Belfast, Northern Ireland.

The facilities of Penn State will be utilized, including those of the College of Science, in addition to housing and food services. The total fee for the three-day session will be $35. In order to insure that each participant will receive full benefit of attendance, and in view of the limited laboratory space available, it will be necessary to limit attendance. Interested persons are urged to register early to insure their participation.

For further information regarding registration and housing write to:

Mr. David R. Schuckers
J. Orvis Keller Conference Center
The Pennsylvania State University
University Park, Pennsylvania 16802

For further information regarding the programme write to:

Mr. Howard J. Francis, Jr.
Pennsalt Chemicals Corporation
900 First Avenue
King of Prussia, Pennsylvania 19406

ENGLAND

INTERNATIONAL SYMPOSIUM ON ANALYTICAL CHEMISTRY, BIRMINGHAM, 1969

21–25 July 1969

The Midlands Section of the Society for Analytical Chemistry is organizing an International Symposium at the University, Birmingham, England, over the period 21–25 July 1969. The programme will include invited and contributed papers covering a wide field of analytical chemistry, together with social events, a ladies' programme, *etc.* Some preliminary notices gave the date of this Symposium as 6–10 April 1970, but this has now been changed to that above.

General information about the Symposium can be obtained from Mr. D. M. Peake, Research Department, Imperial Metal Industries Limited, P.O. Box 216, Witton, Birmingham 6, England. Information about the scientific programme is obtainable from Dr. W. I. Stephen, Department of Chemistry, The University, Birmingham 15, P.O. Box 363, England.

Talanta, 1968, Vol. 15, p. xi. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Aspects of analytical chemistry: R. A. Chalmers. Oliver and Boyd, Edinburgh, 1968. Pp. vii + 144 7/6.

The author has performed a task that most pedogogical analytical chemists would declare to be most desirable but completely impossible. In a few small pages a reader with some chemical knowledge will find what modern analytical chemistry is about. Classical methods and modern instrumental methods each occupy about one third of the book. The emphasis is on explaining the chemistry in analytical chemistry in simple, clear and accurate terms. Throughout, the importance of accuracy and precision is demonstrated in interesting ways. The general reader may find it tough going, but the student working from an analyst's laboratory guide may discover with pleasure what he's about and those who manage to imply that an analyst is not a chemist and that chemistry has no need of analysis should be forced to read it. The publishers have enhanced their good reputation by producing a paperback with excellent layout, which has reasonable paper and which does not fall apart when opened.

Separation Techniques in Chemistry and Biochemistry: R. A. Keller (ed.). Arnold, London, 1967. Pp. xvi + 415. £5/15/-.

This is a collection of papers delivered at the Nineteenth Annual Summer Symposium on Analytical Chemistry. The content varies widely, some papers being in the form of general reviews while others are detailed accounts of aspects of highly specialized techniques. There are some valuable contributions to the development of gas and thin-layer chromatography, electrophoresis and auto-radiography.

Gas Effluent Analysis: William Lodding (ed.). Arnold, London, 1967. Pp. xi + 220. £4/15/-.

Gas effluent analysis as defined in this book appears to be the identification and determination of gases and vapours evolved during the heating of samples. It is thus very widespread in application and may be considered as an extension to differential thermal analysis and thermogravimetry in which weight and temperature changes are related to chemical decompositions. The methods of measurement and identification which are described include gas chromatography, mass spectrometry, thermal conductivity measurement and infrared spectrophotometry. The text is profusely illustrated with explanatory diagrams.

L'analyse par Activation: J. Perdijon. Masson, Paris, 1967. Pp. 156. 68F.

This is a brief but highly priced monograph on the subject of neutron activation analysis and gamma-ray spectrometry. Material includes a theoretical introduction, an account of experimental methods for qualitative and quantitative analysis and an appendix with some useful tables of physical constants.

Talanta, 1968, Vol. 15, p. xi. Pergamon Press. Printed in Northern Ireland

ERRATUM

N. Jordanov, St. Mareva, G. Borisov and B. Jordanov: Substituted phosphonic acid esters as reagents for the separation of molybdenum from rhenium by solvent extraction, *Talanta*, 1968, **15**, 221–227.

Page 226, figure 4: △-I(P-HNEPh); ○-IV(P-NMPh) should read ○—I(P-HNEPh); △—IV(P-NMPh)

Talanta 1968 Vol 15, pp. xi to xii. Pergamon Press. Printed in Northern Ireland

ERRATA

The authors of "High-speed computers as a supplement to graphical methods—V" in the November issue (1967) wish to make the following corrections to the program.

p. 1274 **switch** TRYCKA—insert comma after Tryck 9 at end of line
procedure Cber—last line, change "−23" to "−40"

p. 1275 **procedure** Lnaber—change "**do not if**" to "**do if not**" in line 4
NYKO—add semicolon after **end** in line 7

p. 1276 change "**or**" to "**and**" in line 16

p. 1277 insert semicolon after **end** in line 17 of HOPP

p. 1278 MERTRYCK—delete semicolon after SLUTTRYCK in line 2
SLINGOR—change i: =iva[Rva] to ia: =iva[Rva] in first line

p. 1280 Between lines 5 and 6 (*i.e.* before BEFALL) add three first lines from SING, p. 1280, "**if not** Singfall . . . Nut. =0 **end**;" after that, add; "**if** Nfall > Nva **then begin** Singfall =**true**; Nut. =Nfall−Nva−1; **goto** UPPNUT **end**;"
"SING"—After removal of three lines, only one line is left:

SING: i: =0, Singfall: =**true**;

p. 1280 INFUT—replace line 2 with **for** i. =1 **step** 1 **until** Nut **do** Fall[ifspar[Fut[i]]]: =**false**;

There are also corrections to the text and to the examples given in Table III.

p. 1263 THE PROGRAM, first line, add footnote, attached to "in ALGOL 60".
Footnote: "With the exception that the multiplication sign is written * (asterisk) instead of × (thin cross)".

p. 1269 The footnote should read "The symbol * written on the line stands for multiply."

p. 1282 Line 2 from below, change "50 ml" to "100 ml".

p. 1283 The second line of Input II of example (3*a*) should read
2,1,2,2,6,−3,−3,3,−3,5, (print log a_2 = log [H^+], log a_1,

p. 1284 (3*d*) Input (III:1), change "3(*Ns*)" to "1(*Ns*)".

p. 1286 "Zusammenfassung", last line, change "erscheint" to "erscheinen".
"Resumé", last three lines, change "laquelle" to "lesquelles" and "peut" to "peuvent".

The following text should be added at the end of the paper.

The present program, which consists of one big block, has worked well with the Algol compilers of SAAB D21, CDC3200 and CDC3600. Those who have compilers with a more limited capacity will find it easy to divide the program into seven blocks, NYKO, NYSA, PLAN, NYP, SLINGOR, FALLPROV and NOG, each with its own switches and procedures. To jump from NOG via Sump to ADA, one may, for instance, introduce a new Boolean. In the output for some problems, some of the last digits may vary from one machine to another, depending on the tolerance limits given.

To deal with the unusual case of Nva = 0 (no equation to solve), one may change, at "Nyai" **if** ia > Na **then goto** SLINGOR;" to "**if** ia > Na **then begin if** Nva = 0 **then begin** ivar: =Na + 1; lna[ivar]: =0; Lnbas; Cber; **goto** FALLPROV **end else goto** SLINGOR **end**;".

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NOTICE

TWELFTH CONFERENCE ON ANALYTICAL CHEMISTRY IN NUCLEAR TECHNOLOGY

Mountain View Hotel and Motor Lodge
Gatlinburg, Tennessee
8–10 October 1968

The theme of the Conference is "The Role of the Analytical Chemist: (1) in Research on the Production and Chemical Properties of the Actinide Elements, and (2) in the Elucidation and Solution of Problems in the Field of Environmental Pollution and Related Areas." Papers, up to 25 min in length, that describe original, unpublished work on the following topics are solicited by the Programme Committee.

Analytical Chemistry of the Actinide Elements

1. Ionic methods of analysis.
2. Radiochemical methods of analysis.
3. New methods or techniques potentially useful to the analytical chemist—improved nuclear measurements, methods of separation, and other useful processes.
4. Special facilities and equipment that have been developed and tested in actual operations.

Environmental Pollution and Related Areas

Participation in the sessions on Environmental Pollution will be on an invited-paper basis. However, a limited number of papers are solicited on the following topics.

1. Identification of environmental hazards in water.
2. Identification of environmental hazards in the atmosphere.
3. Criteria and standards for environmental quality and control.

General information

Abstracts. Those who wish to make contributions should submit an abstract of 200–500 words not later than 1 July 1968. The title, name(s) of the author(s), an estimate of the time required for presentation, and the name of the speaker should accompany the abstract. Abstracts and inquiries should be directed to the Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee 37830, U.S.A., Attention: L. J. Brady, Chairman.

Registration fee. The registration fee, except for full-time students, is $5.00 per person.

Reservations. Reservations for lodging should be made by direct communication with: The Mountain View Hotel and Motor Lodge, Gatlinburg, Tennessee 37738.

Talanta, 1968, Vol. 15, p. xiv. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Colorimetric methods of analysis, 3rd Ed. Vol. IV A: FOSTER DEE SNELL and CORNELIA T. SNELL Van Nostrand, London, 1967. Pp. ix + 645. £7

This volume deals with the colorimetric methods of analysis of organic compounds of noncyclic and cyclic nitrogen, proposed between 1953 and 1965. The style and presentation is essentially the same as that used so successfully by the authors in earlier editions. Those concerned with the determination of organic nitrites, nitrates, nitro compounds, amines, proteins, azo compounds *etc.* will find the work of great value.

Paper Chromatography and Electrophoresis, Vol. 1 Electrophoresis in Stabilizing Media: Academic Press, New York, 1967. Pp. xii + 420. £6:12/-.

This volume is on electrophoresis and a companion volume is to appear dealing with paper chromatography, written by G. Zweig. Together they will supplant the 1958 compendium on the two fields by Block, Durrum and Zweig. The present volume contains much new material although little after 1964. It will prove extremely valuable as a general reference book and is well produced. It is a pity that the fairly lengthy index inadequately directs the reader to certain of the topics, for example to sections on ion-exchange, ion-focusing and thin-layer electrophoresis which lie submerged in chapters devoted to particular classes of compounds. After an introductory chapter on methods there are others on Amines, Amino-acids and peptides, Proteins, Nucleic acids and related compounds, Carbohydrates, Organic acids and their derivatives, Inorganic ions, and on other compounds.

Particle Size Analysis, Proceedings of a Conference organized by The Society For Analytical Chemistry and held at Loughborough University of Technology 14–16 September 1966. Society For Analytical Chemistry, London, 1967. Pp. 368 + viii. £7.7.

This collection of papers provides a very useful survey of modern methods in particle size analysis. Material is presented dealing with manual and automatic counting, microscopy and electron microscopy, sedimentation and gas permeability methods. The techniques are applied to a number of industrial problems including those encountered in photography, aerosol sprays, pigments and mineral powders and atomic energy. There are some interesting details on methods of centrifugal sedimentation.

Mass Spectrometry of Organic Compounds: HERBERT BUDZIKIEWICZ, CARL DJERASSI and DUDLEY H. WILLIAMS, Holden-Day, San Francisco, 1967. Pp. xv + 690.

In view of the ever increasing involvement of the organic chemist in the technique of mass spectrometry, this is a most timely and welcome book. The reader is introduced to the most up-to-date methods of structure determination by mass spectrometry and to present views upon the interpretation of the cracking patterns of organic compounds. There follows a very comprehensive discussion of the mass spectra of a wide range of organic compounds including those of phosphorus. The text has been made as up-to-date as possible and the section dealing with organo-metallic compounds contains references only a few months old. The authors are to be congratulated upon making such an extensive and valuable collation.